FINAL REPORT

Development of an Expanded, High-Reliability Cost and Performance Database for In-Situ Remediation Technologies

ESTCP Project ER-201120

MARCH 2016

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To make this large investment in groundwater remediation technologies more effective, end-users need quantitative, accurate, and reliable performance and cost data for commonly used remediation technologies. While the data from an individual site are valuable in guiding site-specific decisions, the real value for the remediation community as a whole is in compiling and analyzing data from a range of sites to provide insight on the overall performance of technologies. The overall objective of this work was to develop a comprehensive remediation performance and cost database.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

ACRONYMS

AFB	Air Force Base
AMIBA	Aqueous and Mineral Intrinsic Bioremediation Assessment
CSU	Colorado State University
CVOC	Chlorinated Volatile Organic Compound
DCE	Dichloroethene
DNAPL	Dense Non-Aqueous Phase Liquid
DoD	Department of Defense
DRA	Driving Range Area
EAB	Enhanced Anaerobic Bioremediation
ESTCP	Environmental Security Technology Certification Program
FTA	Fire Training Area
GSI	GSI Environmental Inc.
GW	Groundwater
HASP	Health and Safety Plan
HPT	Hydraulic Profiling Tool
MNA	Monitored Natural Attenuation
OoM	Order of Magnitude
PBOC	Potentially-Bioavailable Organic Carbon
PCE	Tetrachloroethene
SERDP	Strategic Environmental Research and Development Program
TOC	Total Organic Carbon
TCA	1,1,1-Trichloroethane
TCE	Trichloroethene
USCS	Universal Soil Classification System
VOC	Volatile Organic Compound

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EXECUTIVE SUMMARY

OBJECTIVES

The overall objective of this work was to develop a comprehensive remediation performance and cost database. Key project objectives were as follows:

- Expand an existing performance and cost database (developed as part of SERDP ER-1292) to include more sites and longer post-remediation monitoring periods;
- Examine longer-term datasets to determine whether patterns in sustained treatment and rebound are consistent with findings from our previous work;
- Explore key factors that may contribute to, or affect, remediation performance, sustained treatment, and rebound;
- Explore the potential benefits of successive applications of different remediation technologies, or "treatment train" sites;
- Examine 3 to 4 remediation projects described in the peer-reviewed literature, to evaluate the performance for "remediation-done-right" sites;
- Execute a field program at several sites to collect additional post-remediation monitoring data to fill in gaps related to long-term performance, rebound, and secondary water quality impacts; and

The project met these objectives, with the resulting performance database of 235 sites that suggests that concentration reductions of 0.5 to 2.0 orders of magnitude are typical when using the most common in-situ remedial technologies for groundwater treatment of chlorinated solvents.

BACKGROUND AND METHODOLOGY

The DoD and private sector have invested billions in environmental restoration, with thousands of sites in the United States requiring some type of groundwater remediation. In the process of remediating these sites, large amounts of monitoring data are collected, including prior to the start of clean-up (to characterize the extent of impacts and to provide a baseline for measuring performance), during the active remediation phase (to determine if process modifications are necessary), and after remediation efforts have been completed (to assess performance and progress towards compliance goals). To make this large investment in groundwater remediation technologies more effective, end-users need quantitative, accurate, and reliable performance and cost data for commonly used remediation technologies. While the data from an individual site are valuable in guiding site-specific decisions, the real value for the remediation community as a whole is in compiling and analyzing data from a range of sites to provide insight on the overall performance of technologies.

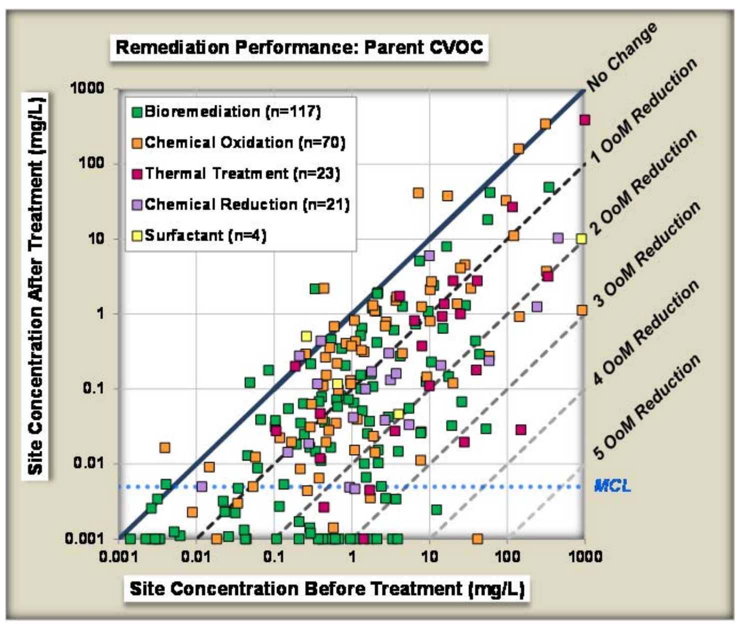
The project consisted of two primary components:

1) Data mining and analysis to extract meaningful remediation performance and cost information from a large number of sites. Several sources of data were identified and used to extract data on the following technologies: i) enhanced bioremediation (117 sites); ii) chemical oxidation (70 sites); iii) thermal treatment (23 sites); iv) chemical reduction (21 sites); v) surfactant flushing (4 sites); and vi) MNA (45 sites). The methodology for assessing performance involved separating actual concentration data from each well at a site into before treatment and after treatment time periods. Next the geometric mean of each time period was calculated resulting in a single "before" concentration and a single "after" concentration for each well. The before and after data points from multiple wells were further reduced by calculating the median value. This produced a single before treatment concentration and a single after treatment concentration for each site. From these before and after treatment concentration values for each site, the *Order of Magnitude* (OoM) reduction achieved by the remedial technology was calculated using the equation below to result in a single performance metric for each site.

2) Focused field studies aimed at generating detailed, long-term post-remediation performance data at a small number of sites where some of the most commonly utilized technologies were applied in various permutations, but in similar hydrogeologic settings. These studies were completed at Altus AFB and Tinker AFB at areas where enhanced bioremediation or chemical oxidation were used 5 to 10 years ago.

KEY RESULTS

- The performance of in-situ CVOC remediation performance technologies at individual sites varies widely, from increasing by about 1 OoM to more than 4 OoM reduction in concentration.
- The middle 50% of the remediation projects achieved between 0.5 and 2 OoMs reduction in the geometric mean of the parent compound (between 71% and 99% reduction), with the median reduction at about **1.1 OoM (91% reduction).** Additional percentile results are summarized in the table below.



Remediation Performance of 235 In-Situ CVOC Remediation Projects

- Remediation performance is generally poorer when site maximums are used as the performance metric compared to geomeans. The exception was chemical oxidation, which

showed better performance when using maximums (median OoM reduction of 1.0 using maximums vs. 0.63 using geomeans).

Percentile of 235 Active In-Situ Remediation Projects	% Reduction in Geomean of Parent Compound in Treatment Zone	OoM Reduction in Geomean of Parent Compound in Treatment Zone
90%	99.8%	2.7
75%	98.9%	2.0
50%	91.2%	**1.1**
25%	71.4%	0.5
10%	30.8%	0.2

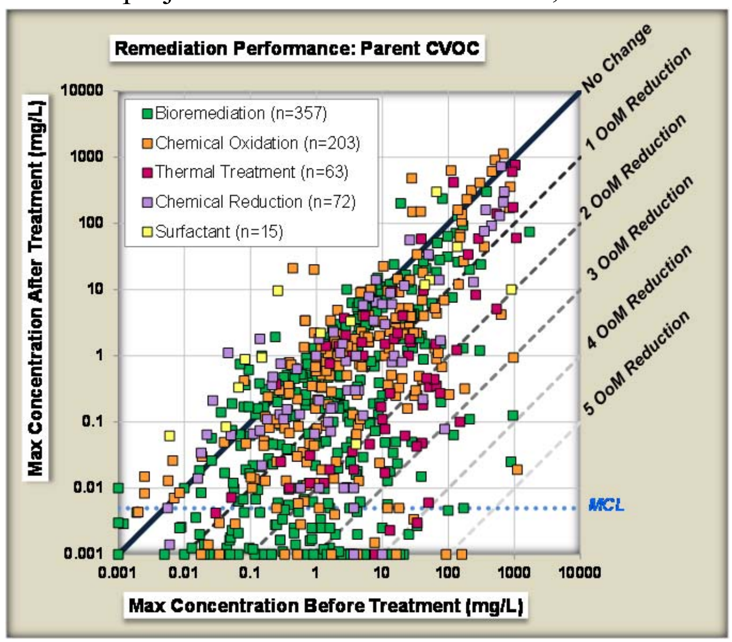
- When using site maximums, the middle 50% of all remediation projects achieved between **0.2 and 1.4 OoMs** reduction in the site maximum concentration of the parent compound (between 41% and 96% reduction), with the median reduction at about 0.8 OoM (84% reduction). By comparison, when using geomeans for evaluating performance, the middle 50% range of all projects was **0.5 to 2 OoMs**, with a median of 1.1 OoMs (see Table 4.2).
- When considering *geomean* concentrations for the *parent* compound, there does not appear to be significant differences in the performance of the four main technologies. Chemical oxidation appeared to have the worst performance (lowest OoM reduction) and thermal the best, but this is not statistically significant.

	Parent Median Geomean Before (mg/L)	Parent Median Geomean After (mg/L)	% Reduction in Parent Concentration	OoM Reduction in Parent Concentration*
Bioremediation (n=117)	0.74	0.027	96%	**1.4**
Chemical Oxidation (n=70)	1.1	0.27	77%	**0.6**
Thermal Treatment (n=23)	10	0.20	98%	**1.7**
Chemical Reduction (n=21)	1.8	0.13	93%	**1.1**

- In a comprehensive statistical comparison of how different technologies performed, there were only few instances where a difference was indicated, and most of these suggested that the median of chemical oxidation was less than the respective value for the comparative technology. However, the major finding from this analysis was a confirmation that the four major technologies generally achieve similar results.
- No significant differences in performance were observed for different variations within a technology (e.g., soluble vs. slow-release substrates for bioremediation, permanganate vs. peroxide/Fenton's for chemical oxidation).
- Poorer performance was generally observed when the Total CVOC was the contaminant metric, particularly for bioremediation because this technology converts parent compounds to daughter products, and is generally less efficient at removing the lower chlorinated CVOCs (as is chemical reduction). Chemical oxidation projects were least impacted when *Total*

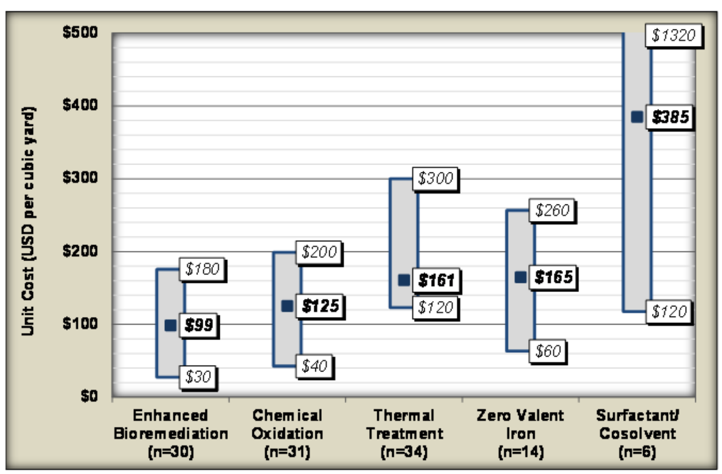
CVOC concentrations were used compared to the *parent compound concentration.* This is expected as chemical oxidation does not result in the production of daughter products.

- The performance for all in-situ remediation projects was similar for sites with PCE as the parent compound, TCE as the parent compound, and 1,1,1-TCA as the parent compound.
- One well-accepted design rule for in-situ remediation projects is that treatment is easier (and performance supposedly better) for sites with more permeability and homogeneity, and that treatment of fractured rock sites is significantly more difficult than unconsolidated sites. However the performance data from this project did not see this effect; the overall performance of fine-grained sites *as defined by the available data* is comparable to coarse grained sites.
- Performance was relatively consistent across the treatment durations reported for the 235 projects. However, projects with a treatment duration exceeding 1 year performed slightly better than those with less than 1 year of treatment duration.
- Only 21% of 710 monitoring wells at 235 sites achieved a typical MCL of 0.005 mg/L based on maximum concentrations after treatment (Table 4.7a). Only 7% of 235 sites achieved MCLs at every monitoring well for the parent CVOC (Table 4.7a).



Change in Maximum Parent Compound Concentration for All 710 Wells Analyzed for this Project.

- The unit costs for a typical in-situ remediation project ranges between $100 and $300 per cubic yard, but with some projects below $10 and some over $1000 per cubic yard (see figure to the right). The median thermal project (n=34) was about 50% more expensive than enhanced bioremediation and chemical oxidation projects. The performance of a remediation project did not seem to be correlated to unit costs. This is surprising, as more resources suggest more intense treatment that should translate to higher performance. But the remediation projects in this database may reflect costs that deal with

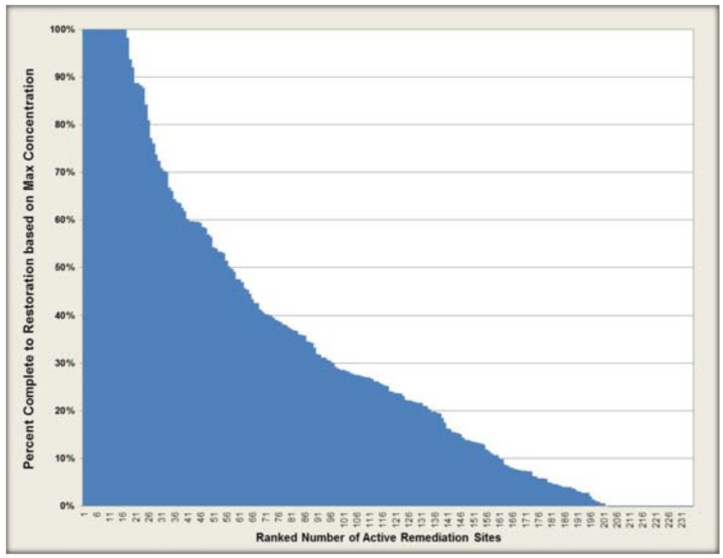


external factors, such as access, high concentrations, difficult hydrogeologic conditions, and therefore unit cost for treatment may not correlate to outcome at many sites.

- At sites with longer monitoring records, the occurrence of concentration rebound and sustained treatment during the post-treatment period was evaluated. Results demonstrated the concentration rebound was more common at chemical oxidation sites with about 30% of all wells showing rebound. Sustained treatment appeared to be occurring for at least 3 to 12 years after treatment at about 65 to75% of bioremediation sites.

- Remediation performance was evaluated relative to numerous site and remediation characteristics (geology, size, depth, number of monitoring wells, etc.) to determine if correlations could be used as a predictor of performance. No strong correlations were found.

- A metric was derived to calculate the "Percent Complete to Restoration" of groundwater (see figure to the right). The calculation is based on maximum concentrations remaining in groundwater after treatment and the typical groundwater MCL of 0.005 mg/L. Results indicate that current practice as reflected in the 235-site database typically achieves between 6% and 48% Complete to Restoration, with a median of 25%. Only about 7% of the 235 sites achieved 100% Complete to Restoration.



- 14 sites in the database implemented multiple technologies in successive treatments or "treatment trains." Overall the treatment train sites achieved about a 2.3 OoM reduction based on the median of all 14 sites. This is significantly higher than the median OoM reduction of 1.1, as well as the 75th percentile of 2.0 OoM, observed for all 235 of the remediation projects. Based on the poorer OoM reduction typically achieved by the first technology at these sites, it is likely that a key factor in the success of the second technology was the benefit of lessons learned from the first technology implementation.

- Long-term follow-up sampling was performed for 5 remediation projects that were previously conducted at Tinker AFB and Altus AFB. The objective was to further evaluate long-term concentration trends following in-situ remediation. Results demonstrated that sustained treatment was still occurring 5 to 10 years after treatment at 2 bioremediation sites where a slow-release substrate was used. Concentrations had rebounded to pre-treatment levels at 1 bioremediation site where a soluble substrate was used. For the 2 chemical oxidation sites tested, 1 site rebounded to near pre-treatment levels, while concentrations remained depressed at the other site.

- To get an independent perspective on in-situ remediation performance, a review of three well-implemented, well-reported, peer-reviewed remediation projects was performed. These

projects represent "remediation done right" for individual one-phase treatment projects (i.e., treatment trains are excluded from this analysis). The objective was to evaluate the performance for well-designed, well executed, and well-documented in-situ remediation projects in the scientific literature. The results reported for these three projects indicated that two of three outperformed many of the sites in the 235 site database (achieving parent CVOC reductions of 2.7 and 3.5 OoMs), while the third site had a result more comparable to the median of the 235 site dataset with a 0.8 OoM reduction.

- An Expert Panel was convened to review the project methods and findings. Overall, the experts concluded that the project data were useful for remedial decision-making and that the findings provided a useful "Range of Expectations." They stressed a tiered relevance, where the data will be very useful for technology screening, supportive for the conceptual design, and less useful at the detailed design stage. The Panel agreed that use of geometric mean concentrations was appropriate for determining representative groundwater conditions, but that evaluation of maximum concentrations remains important from a regulatory perspective. Additional feedback from the Expert Panel is provided in Appendix A.

PERFORMANCE OBJECTIVES

The following tables describe the performance objectives developed for the data mining portion of the project. Additional objectives were developed for the field demonstration and are described in Section 3. All performance objectives were successfully achieved.

Performance Objective	Data Requirements	Success Criteria	Success Criteria Achieved?
Quantitative Performance Objectives			
Expand number of temporal records in database	Temporal records (concentration vs. time) at wells from new sites that were not part of the SERDP ER-1292 database	Add 30 sites to original database, representing an increase of 50% from original database	***YES: Added 176 new sites***
Expand length of temporal records in database	Updated temporal records (concentration vs. time) at wells that were included the SERDP ER-1292 database	Add 3 to 5 years of data for temporal records from 15 sites in original database, representing an increase of ~50% in the overall average temporal record length	***YES: 2 to 10 years (avg. of 6.1 years) of additional data added for 15 sites***
Qualitative Performance Objectives			
Ease of Data Collection Efforts	Feedback from site managers/agencies	Response from sufficient number of site managers	***YES: 134 new sites added electronically from online data sources***

IMPLEMENTATION

The final products of this project include numerous charts and graphics that are intended to help inform the remedial decision-making process at sites, as well as an electronic Decision Support System that allows the user to select various site parameters and remedial technologies to see the actual remediation performance data for sites with the selected characteristics. In no case is the dataset intended to replace a thorough technology screening, design, and/or feasibility or pilot testing. Furthermore, the dataset is not intended to predict precisely what remediation outcome might be achieved at a specific site, but rather to provide a range of expectations based on levels of performance that were achieved at other sites with similar characteristics.

We expect that the dataset contained herein will have a tiered relevance as part of the remedial decision-making process, where the data will be very useful for technology screening, supportive for the conceptual design, and less useful at the detailed design stage. For sites that are already undergoing active remediation, we envision that the dataset could be particularly useful for transition assessments at complex sites and for Five-Year Reviews at federal cleanup sites.

1.0 INTRODUCTION

This document serves as the final report for ESTCP Project Number ER-201120, "**Development of an Expanded, High-Reliability Cost and Performance Database for In-Situ Remediation Technologies**". It was prepared in accordance with ESTCP program guidance by the Principal Investigators for this project, GSI Environmental Inc. (GSI).

1.1 Background

The DoD and private sector have invested billions in environmental restoration, with thousands of sites in the United States requiring some type of groundwater remediation. To make this large investment in groundwater remediation technologies more effective, end-users need quantitative, accurate, and reliable performance and cost data for commonly used remediation technologies. The U.S. EPA cited this as a "primary research need" in the 2003 DNAPL Expert Panel document (Kavanaugh et al., 2003), and concluded:

> *"the degree of uncertainty in the costs and benefits of applying source depletion technologies is currently at levels that discourage widespread use of the available source depletion technologies at DNAPL sites," and*
>
> *"such documentation would provide important insights on the benefits that could be achieved even with partial DNAPL source depletion."*

More recently, the National Research Council, in their report on *Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites* (NRC, 2013), stated that:

> *"The Committee could identify only limited data upon which to base a scientifically supportable comparison of remedial technology performance,"*
>
> *"Adequate performance documentation generated throughout the remedial history at sites either is not available or does not exist for the majority of completed remediation efforts," and*
>
> *"There is a clear need for publically accessible databases that could be used to compare the performance of remedial technologies at complex sites (performance data could be concentration reduction, mass discharge reduction, cost, time to attain drinking water standards, etc.)"*

Large amounts of monitoring data are collected as part of all remediation projects, including prior to the start of clean-up (to characterize the extent of impacts and to provide a baseline for measuring performance), during the active remediation phase (to determine if process modifications are necessary), and after remediation efforts have been completed (to assess performance and progress towards compliance goals). Monitoring-related expenditures can easily exceed the actual cost of clean-up at some sites. While the data from an individual site are

valuable in guiding site-specific decisions, the real value for the remediation community as a whole is in compiling and analyzing data from a range of sites to provide insight on the overall performance of technologies. In effect, data mining leverages the money already spent for monitoring during past remediation projects, thereby providing a sounder basis for future financial decisions at other sites.

As part of a SERDP-funded project (ER-1292), GSI compiled a detailed historical database on the performance and costs of source depletion technologies. This cost and performance database was the highest quality dataset assembled to date (based on the data density and publication of peer-reviewed papers). The project represented the first rigorous, independent performance evaluation of four commonly utilized remediation technologies: enhanced bioremediation, chemical oxidation, surfactant/cosolvent flushing, and thermal treatment. Key findings from the project were disseminated via publications in scientific journals and these publications, listed below, were in turn heavily cited in the literature:

- Remediation Performance at 59 Sites: McGuire et al., 2006 (108 Google Scholar citations)
- Remediation Cost at 36 Sites: McDade et al., 2005 (33 Google Scholar citations)
- Source Attenuation Rates at 23 sites: Newell et al., 2006 (33 Google Scholar citations)
- Source Decay Models: Newell and Adamson, 2005 (25 Google Scholar citations)

The extensive utilization of this dataset was evidence that the remediation community has an essential need for high-quality, reliable remediation performance and cost data.

1.2 Objective of the Demonstration

The overall objective of this work was to expand the breadth and depth of the remediation performance and cost database compiled as part of the previous SERDP project (ER-1292) to provide a more powerful and reliable dataset.

Specific project objectives were as follows:

- Expand the existing performance and cost database to include more sites and longer post-remediation monitoring periods;
- Examine longer-term datasets to determine whether patterns in sustained treatment and rebound are consistent with findings from our previous work;
- Explore key factors that may contribute to, or affect, remediation performance, sustained treatment, and rebound;
- Evaluate and add performance data from existing technology-specific ESTCP performance studies;
- Explore the potential benefits of successive applications of different remediation technologies, or “treatment train” sites;

- Examine 3 to 4 remediation projects described in the peer-reviewed literature, to evaluate the performance for "remediation-done-right" sites;
- Execute a field program at 3 to 4 sites to collect additional post-remediation monitoring data to fill in gaps related to long-term performance, rebound, and secondary water quality impacts; and
- Expand the SERDP Decision Support System software with the results of the study.

The final products of this project include numerous charts and graphics that are intended to help inform the remedial decision-making process at sites, as well as an electronic Decision Support System that allows the user to select various site parameters and remedial technologies to see the actual remediation performance data for sites with the selected characteristics. In no case is the dataset intended to replace a thorough technology screening, design, and/or feasibility or pilot testing. Furthermore, the dataset is not intended to predict precisely what remediation outcome might be achieved at a specific site, but rather to provide a range of expectations based on levels of performance that were achieved at other sites with similar characteristics.

We expect that the dataset contained herein will have a tiered relevance as part of the remedial decision-making process, where the data will be very useful for technology screening, supportive for the conceptual design, and less useful at the detailed design stage. For sites that are already undergoing active remediation, we envision that the dataset could be particularly useful for transition assessments at complex sites and for Five-Year Reviews at federal cleanup sites.

1.3 Regulatory Drivers

Regulatory cleanup requirements are a primary driver for most groundwater remediation projects. At many sites, restoring groundwater to a potentially-usable source of drinking water is the ultimate goal, requiring that contaminant concentrations be remediated below the federal primary drinking water standards, or Maximum Contaminant Levels (MCLs). For chlorinated solvents, which were the focus contaminants for this project, the MCLs are typically two to five *Orders of Magnitude* lower than groundwater concentrations commonly encountered in source zones, as depicted on Figure 1.1.

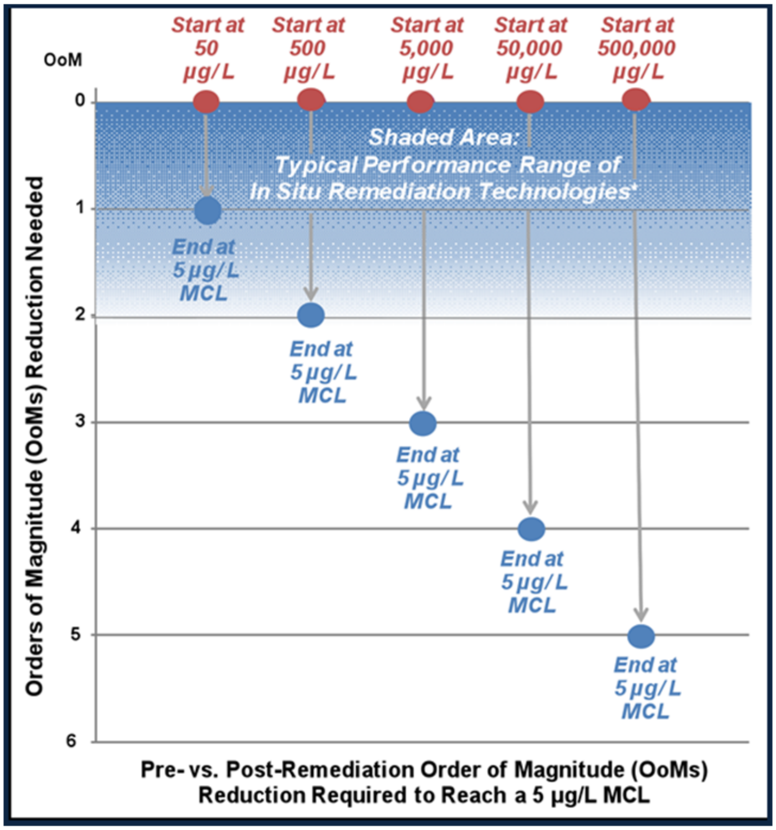


Figure 1.1: Order of Magnitude Reduction Required to Reach a 5 ug/L MCL (from ITRC, 2011; derived from Sale et al., 2008).

** Typical Performance Range of In-Situ Remediation Technologies in this graphic was based on the findings of our previous SERDP study as reported in McGuire et al., 2006.*

2.0 TECHNOLOGY

2.1 Technology Description

The project consisted of two primary components: i) data mining and analysis to extract meaningful remediation performance and cost information from a large number of sites; and ii) focused field studies aimed at generating detailed, long-term post-remediation performance data at a small number of sites where some of the most commonly utilized technologies were applied in various permutations, but in similar hydrogeologic settings. Each of these is described in more detail in the sections below.

2.2 Data Mining

Data mining works on the simple principle that the more data that are available to be compiled and analyzed (especially if the data originated from multiple sources), the more powerful are the conclusions that can be made. Data mining allows a user to test a hypothesis, or alternatively, to develop new hypotheses based on patterns that may not have been previously apparent.

2.2.1 Technologies

The data mining project focused on in-situ groundwater remediation technologies, with a secondary emphasis on untreated (natural attenuation) sites. Ex-situ technologies (e.g., excavation and off-site disposal), containment technologies (e.g., pump-and-treat), and soil-focused remediation technologies (e.g., soil vapor extraction) were excluded, though sites where one of these technologies had been applied in the past did not necessarily result in exclusion of the site from further consideration. To the extent practicable, efforts were made to exclude sites or portions of sites where these other technologies appeared to have affected the performance of the in-situ groundwater remediation technology.

The groundwater remediation technologies included in the previous SERDP project were used as the starting point for the technologies to be included in the current work. These technologies, and the number of sites from our previous SERDP project, included:

- Enhanced bioremediation (n=26);
- Chemical oxidation (n=23);
- Thermal treatment (n=6); and
- Surfactant/cosolvent flushing (n=4).

To evaluate whether technologies should be added or removed from the list above, a preliminary data mining step was conducted to identify the most commonly applied technologies for groundwater remediation. First, a keyword search was performed using Google Scholar to assess the frequency of citations relating to various technologies over time. The keyword search

included the terms "chlorinated solvent," "groundwater," and the remediation technology. The results are shown in Figure 2.1.

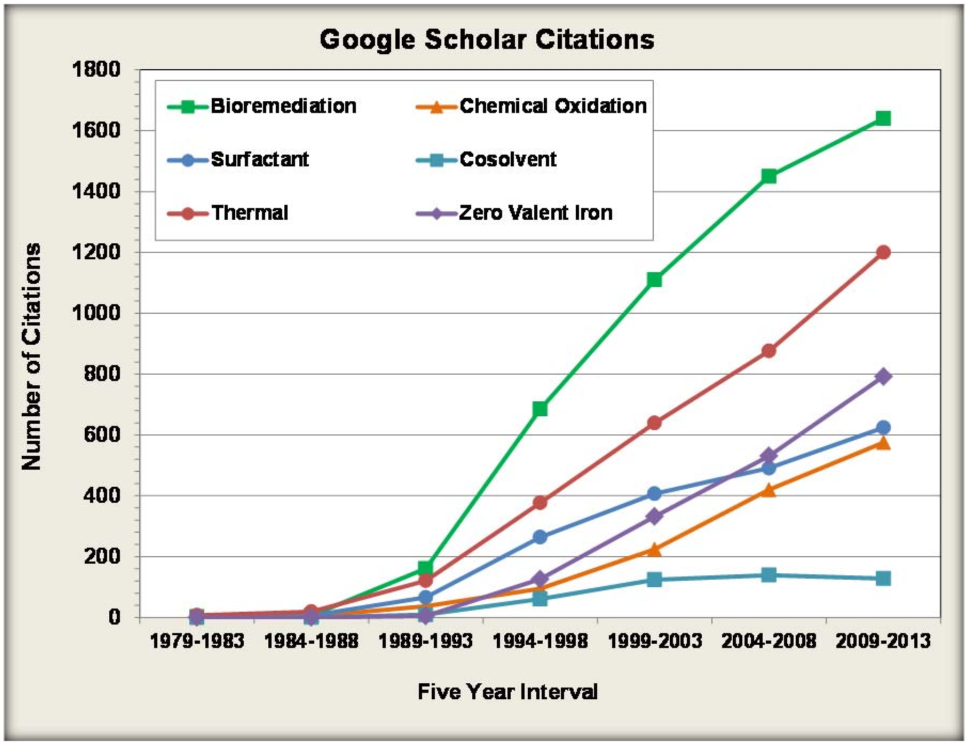


Figure 2.1. Technology Applications over Time based on Google Scholar Citations.

Next, the frequency of technology use according to the Superfund Remedy Report series was evaluated by calculating the number of technology applications for in-situ source control over five-year periods. The results are shown in Figure 2.2.

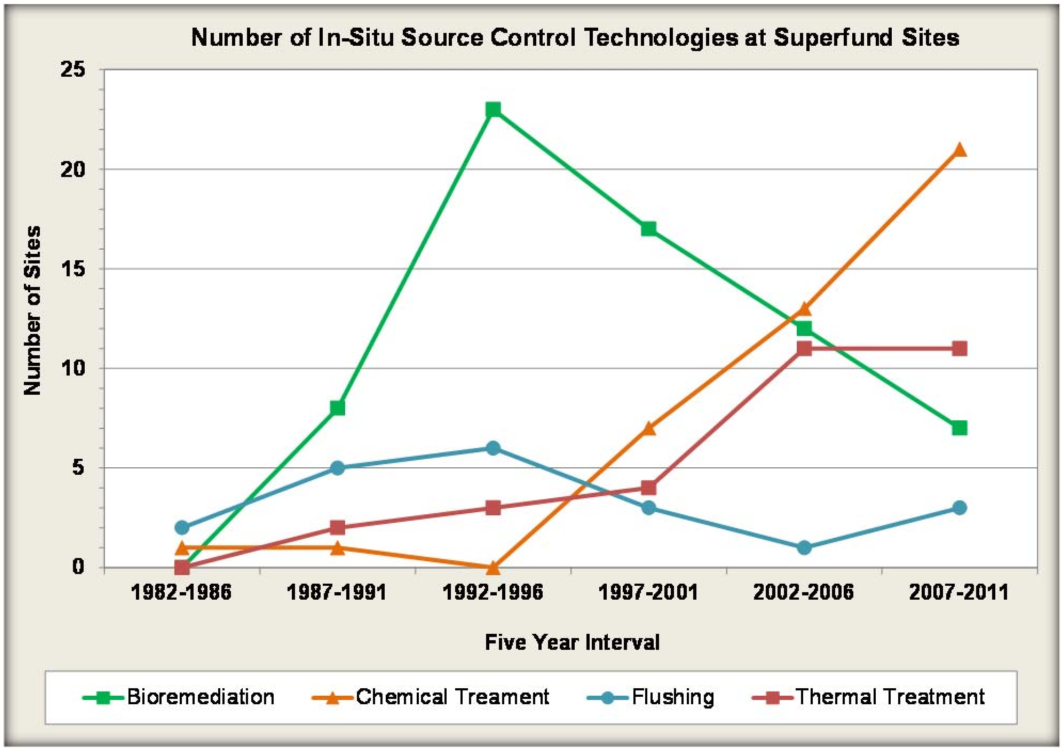


Figure 2.2. Technology Applications over Time based on the Superfund Remedy Report.

Together, these evaluations resulted in several key conclusions:

- Enhanced bioremediation and chemical oxidation remain as important technologies, and though the use of bioremediation has declined at Superfund sites, both of these technologies should continue to be a key focus for our project;
- Thermal treatment appears to be implemented more frequently in recent years, suggesting that more effort should be placed on increasing the number of thermal sites in our database;
- Surfactant/cosolvent flushing technologies have relatively lower incidence of application, and as such less emphasis was placed on data mining this technology in the current study; and
- Chemical reduction (i.e., zero-valent iron on Figure 2.1 and captured by the Chemical Treatment category on Figure 2.2) has an increasing frequency of application, and therefore was added as a new technology.

In sum, the four technologies retained for additional data mining are listed below. The four surfactant sites from the original study were also retained in the database.

- Enhanced bioremediation;
- Chemical oxidation;
- Thermal treatment; and
- Chemical reduction.

In addition to these active remediation technologies, an emphasis was placed on adding more natural attenuation sites to the database as a basis for comparison.

2.2.2 Primary Data Sources

Project data was obtained from multiple sources, including:

- Project surveys completed as part of SERDP project ER-1292;
- Literature reports;
- Reports submitted to regulatory agencies and obtained through internet repositories, on-site file searches, or Freedom of Information Act (FOIA) requests;
- Regulatory databases, including the California GeoTracker database and the Florida Department of Environmental Protection Dry-cleaning Solvent Cleanup Program;
- Technology fact sheets or white papers;
- Other technology performance research studies, including:
    - Thermal treatment by Dr. Paul Johnson, SERDP Project ER-200314 (Kingston et al., 2012);
    - Chemical oxidation by Dr. Robert Siegrist, SERDP Project ER-1290 (Krembs et al., 2010);
    - Chemical reduction by Dr. Silvia Comba, Polytechnic University of Turin (Comba et al., 2011); and
    - Enhanced bioremediation by Dr. Denice Nelson; ARCADIS (Suthersan et al., 2013)

2.2.3 Data Obtained

The critical data that were required for a site to be included in the database consisted of the following parameters:

- Application of one of the technologies listed in Section 2.2.1 for the treatment of chlorinated solvents in groundwater;

- Actual groundwater concentration data from within the treatment zone for the parent compound from before and after treatment (i.e., reported "percent reduction" values were excluded);
- Treatment date(s); and
- For natural attenuation sites, a data record spanning at least four years.

The following information was also obtained if available:

- Site location;
- Concentrations of daughter products over time;
- Specific remedial amendment(s) or configuration applied;
- Map showing treatment well and monitoring well locations;
- Boring logs or cross-sections showing lithology of the treatment zone;
- Area of treatment zone;
- Depth of treatment zone;
- Project scale (full vs. pilot); and
- Cost of the remediation project.

2.2.4 Performance Calculations

The ultimate goal of the data mining effort was to produce a single performance metric for each site based on actual concentration versus time data from one or more wells located within the treatment zone. To achieve this goal, concentration data from each well at a site was separated into before treatment and after treatment time periods. Next the geometric mean of each time period was calculated resulting in a single "before" concentration and a single "after" concentration for each well. The before and after data points from multiple wells were further reduced by calculating the median value. This produced a single before treatment concentration and a single after treatment concentration for each site.

> ***Why Geometric Mean?*** Geometric means are generally applicable for datasets with a log-normal distribution. Groundwater datasets tend to be log-normally distributed, as concentrations often vary over orders of magnitude. Use of the geometric mean "smooths out" some of the natural variability inherent in groundwater data. In Section 4.5, an alternative approach using maximum before and after concentrations is discussed.

From these before and after treatment concentration values for each site, the *Order of Magnitude* (OoM) reduction achieved by the remedial technology was calculated using the equation below to result in a single performance metric for each site.

$$OoM\ Reduction = -\log\left(\frac{C_{after}}{C_{before}}\right)$$

Calculating OoM reduction as the negative logarithm of the after-to-before concentration ratio produces a simple metric with a typical range of 0 to 5, with each integer representing an order-of-magnitude. The method is analogous to calculation of pH or pK_a values in chemistry. OoMs directly correlate to "the number of 9s in percent reduction" as shown on Table 2.1.

Table 2.1. OoM Reduction vs. Percent Reduction

OoM Reduction	Corresponding Percent Reduction
1	90%
2	99%
3	99.9%
4	99.99%
5	99.999%

Percent reduction values can easily be converted to OoM reduction using the following equation, which was presented in the ITRC Integrated DNAPL Site Strategy guidance document (ITRC, 2011):

$$\text{OoM Reduction} = -\log\,[1-(\text{Percent Reduction} \div 100)]$$

For natural attenuation sites, the first year of the monitoring data and the last year of the monitoring data were used in lieu of the "before" and "after" treatment periods discussed above for active remediation sites.

2.2.5 Cost Calculations

Costs associated with remediation projects were extracted from the site information when available. The protocol was similar to that used for an earlier compilation under SERDP ER-1292 (McDade et al., 2005). Quality of the cost information varied from detailed cost breakdowns to lump costs reported for an entire project without details on what was included or excluded. To the extent practicable, only those costs directly associated with the remediation project were included in the cost analysis.

Costs were normalized by the treatment volume (as in-place cubic yards) to allow for more direct comparison between technologies. As such, only sites with both cost information and treatment volume data were included in the cost analysis. Costs associated with natural attenuation projects were not evaluated.

2.2.6 Expert Panel Meeting

An Expert Panel was convened to review the project methods and findings. The panelists were:

- Dr. John Wilson, Scissortail Environmental Solutions;
- Dr. Herb Ward, Rice University; and

- Dr. Tom Sale, Colorado State University

The project team presented details of the project technical approach and results to the Panel. The panel provided feedback and suggestions during the meeting, and were also given the opportunity to provide additional feedback after the meeting.

Overall, the experts concluded that the project data were useful for remedial decision-making and that the findings provided a useful "Range of Expectations." They stressed a tiered relevance, where the data will be very useful for technology screening, supportive for the conceptual design, and less useful at the detailed design stage. The Panel agreed that use of geometric mean concentrations was appropriate for determining representative groundwater conditions, but that evaluation of maximum concentrations remains important from a regulatory perspective. Additional feedback from the Expert Panel is provided in Appendix A.

2.3 Focused Field Studies

Focused field studies were performed at two sites: Tinker Air Force Base (AFB) in Oklahoma City, Oklahoma and Altus AFB in Altus, Oklahoma. The two sites are located approximately 120 miles apart and have similar hydrogeologic settings.

At Tinker AFB, two areas were selected for testing: Fire Training Area 2 (FTA-2) and the Driving Range Area (DRA). At FTA-2, a large-scale enhanced bioremediation pilot test using a slow-release carbon substrate (emulsified soybean oil) was conducted in 2003, with the last sampling event conducted in 2005. At the DRA, a large-scale, multiple technology pilot test was conducted in 2003-2004, with the last sampling event in 2006. The DRA project consisted of three side-by-side treatments including enhanced bioremediation using a soluble carbon substrate (lactate), chemical oxidation using Fenton's reagent, and chemical oxidation using potassium permanganate.

At Altus AFB, the groundwater source area associated with Building 323 was selected for testing. At this site, a full-scale enhanced bioremediation project using a slow-release carbon substrate (emulsified vegetable oil) was implemented in 2008, with the last sampling event in 2011. Table 2.2 summarizes the characteristics of the focused field study testing sites. Additional details of the testing program can be found in the Final Demonstration Plan (GSI, 2013) and in the *ESTCP Field Demonstration Site Investigation Report* provided in Appendix B.

Table 2.2. Characteristics of Focused Field Study Sites

Site ID	Technology	Amendment	Time Since Treatment of GSI Sampling, yrs.
Altus Bldg. 323	Enh. Bio.	Emulsified oil	5
Tinker FTA-2	Enh. Bio.	Emulsified oil	10
Tinker DRA-1	Enh. Bio.	Lactate	10
Tinker DRA-2	Chem. Ox.	Fenton's reagent	10
Tinker DRA-3	Chem. Ox.	Potassium permanganate	10

2.4 Advantages and Limitations

Potential advantages and disadvantages of our dataset, and multi-site studies in general, are listed in Table 2.3 below. Some of these topics are further addressed in Section 4 of this report.

Table 2.3. Advantages and Potential Limitations of Multi-Site Studies

Advantages	Limitations
Researchers are independent of the technologies	Findings are not site-specific
Data analysis methods are repeatable and consistent	Pilot scale projects are mixed with full scale projects
Results cover a broad spectrum of sites	Results may not account for "intentional" shutdowns
Results are based on actual concentration data, not anecdotal information	Results may not account for different levels of design / experience
Numerous multi-site studies have been published in peer-reviewed literature	Results may not account for knowledge gained and better application over time

2.4.1 Use of Groundwater Concentration Data from Monitoring Wells

Groundwater concentration data from monitoring wells within the treatment zone represents the primary performance metric used in this evaluation. The strengths of using concentration data from monitoring wells include:

- Concentration data from monitoring wells is relied upon by regulatory agencies to evaluate the need for cleanup, monitor cleanup progress, and to determine if cleanup goals are met; and
- The groundwater industry is well versed in the collection and interpretation of monitoring well data.

However, there are issues with groundwater monitoring data that can complicate the analysis of remediation performance data, such as:

- Groundwater monitoring data has significant short-term variability (SERDP Project ER-1705; ESTCP Project ER-201209) that can complicate trend analysis and comparisons between data sets;
- There are different methods for well construction (e.g., short screen vs. long screen) and different groundwater sampling methods (e.g., high-volume purge vs. low-volume purge vs. no-purge) that have the potential to introduce bias in different data sets; and
- Groundwater monitoring data alone may not fully capture some site characteristics that can also influence remediation performance, such as: source zone size and architecture, groundwater flow velocity, mass distribution in different phases, and the potential for exposure via other exposure pathways.

This ESTCP project addresses these issues as follows:

Variability is addressed by “averaging” concentrations both temporally (by calculating geomean concentrations of all available monitoring events vs. any single event or narrow window in time) and spatially (by calculating the median geomean concentration for all wells in the treatment zone vs. using only concentration data from a single well) to derive “site concentration” metrics before treatment and after treatment for evaluating remediation performance.

Different methods for well construction and groundwater sampling are largely managed by relying on permanent monitoring wells with long term temporal records, which largely excludes one-time direct push sampling with short well screens. At most of these sites, if there were any changes in sampling methods over time, our experience indicates that such changes were likely approved by site stakeholders with the intention that the quality and consistency of the monitoring record would not be compromised. In addition, ESTCP Project ER-201209 concluded that the sampling method “has only a modest impact on monitoring variability and concentration” in the context of long-term monitoring programs.

3.0 PERFORMANCE OBJECTIVES

Performance objectives for the data mining component and focused field study component are provided in Tables 3.1 and 3.2, respectively, and are discussed in more detailed in the following subsections.

Table 3.1. Performance Objectives for Data Mining

Performance Objective	Data Requirements	Success Criteria	Success Criteria Achieved?
Quantitative Performance Objectives			
Expand number of temporal records in database	Temporal records (concentration vs. time) at wells from new sites that were not part of the SERDP ER-1292 database	Add 30 sites to original database, representing an increase of 50% from original database	***YES: Added 176 new sites***
Expand length of temporal records in database	Updated temporal records (concentration vs. time) at wells that were included the SERDP ER-1292 database	Add 3 to 5 years of data for temporal records from 15 sites in original database, representing an increase of ~50% in the overall average temporal record length	***YES: 2 to 10 years (avg. of 6.1 years) of additional data added for 15 sites***
Qualitative Performance Objectives			
Ease of Data Collection Efforts	Feedback from site managers/agencies	Response from sufficient number of site managers	***YES: 134 new sites added electronically from online data sources***

3.1 Data Mining Performance Objectives

3.1.1 Performance Objective: Expand number of temporal records in database

This performance objective sought to add at least 30 new remediation projects, thus expanding by 50% the 59-site database compiled as part of the previous SERDP project. This objective was far exceeded through the addition of 176 new remediation projects. Note that at 9 of the 59 original sites, a second remediation technology was applied, and these new applications were considered as "new" remediation projects within the database. Performance at these 9 sites, along with another 4 sites where multiple technologies were applied, will be further evaluated in the "treatment train" section of this report.

3.1.2 Performance Objective: Expand length of temporal records in database

This performance objective sought to add 3 to 5 years of new monitoring data for at least 15 sites in the original SERDP database. This objective was exceeded through the addition of 2 to 10 years (with an average of 6.1 years) of new monitoring data for 15 sites from the original database.

3.1.3 Performance Objective: Ease of data collection efforts

This qualitative objective focused on the ability to easily identify and extract remediation data from new and existing sites. At the time this objective was proposed, it was envisioned that much of the data would come from site managers or regulatory contacts, and therefore, would require their direct involvement in providing site data. However, as the project was implemented, we discovered a new primary means to extract data for a large number of sites – online databases and site report repositories. Data for approximately 134 of the 176 new sites were added through electronic means, which is much more efficient than searching through and extracting data from hard copy reports. As such, this performance objective was considered achieved.

3.2 Focused Field Study Performance Objectives

3.2.1 Performance Objective: Collect data to evaluate long-term impacts following in-situ groundwater remediation

The quantitative performance objective for the field demonstration focused on successfully completing the data collection efforts rather than achieving a particular outcome since the overall goal of the project was to evaluate long-term concentration trends and not to demonstrate a particular trend. This objective was achieved through the collection and analysis of all samples as proposed in the Field Demonstration Plan (GSI, 2013).

3.2.2 Performance Objective: Evaluate long-term remediation impacts

This objective specified the data analysis methods that were to be used in the evaluation of long-term remediation impacts based on the data collected as part of the field demonstration. This objective was achieved through the data collection and subsequent data analysis. Details and results of the data analysis are presented in Section 5.0 of this report.

Table 3.2. Performance Objectives for Focused Field Studies

Performance Objective	Data Requirements	Success Criteria	Success Criteria Achieved?
Quantitative Performance Objectives			
Collect data to evaluate long-term impacts following in-situ groundwater remediation	• CVOC concentrations in saturated soil and groundwater • Geochemical concentrations in groundwater • Microbial and mineralogical parameters in saturated soil groundwater	Sample collection at 100% of targeted areas	***YES: Samples collected at all proposed locations***
Qualitative Performance Objectives			
Evaluate long-term remediation impacts	Existing pre-treatment and post-treatment monitoring data, and new long-term post-treatment monitoring data to be collected as part of field demonstration	• Data are sufficient to evaluate long-term CVOC concentration trends as follows: ▪ Determine average post-treatment concentrations including new monitoring data relative to average post-treatment concentrations without the new monitoring data ▪ Determine temporal trends including the new monitoring data relative to trends without the new monitoring data • Data are sufficient to evaluate long-term geochemical changes • Data are sufficient to evaluate microbial and mineralogical conditions	***YES: Data sufficient to evaluate long-term concentration trends***

4.0 DATA MINING RESULTS

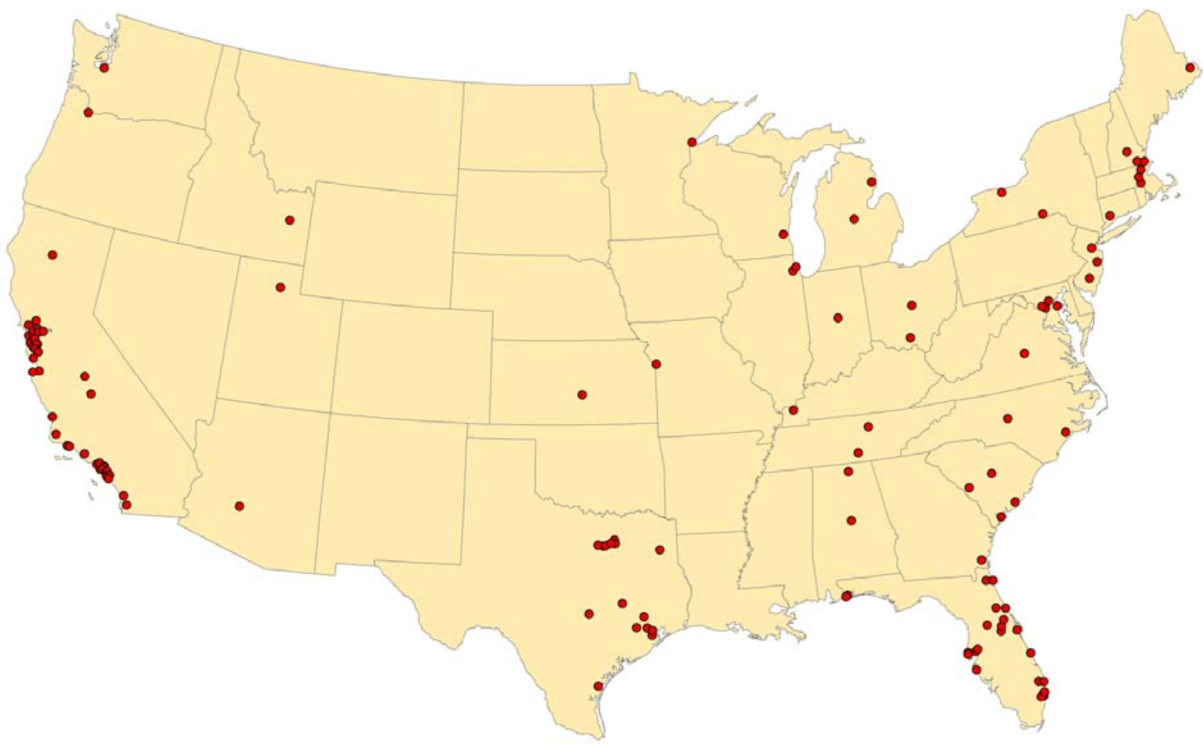
4.1 Overview of the Database

The project team reviewed thousands of pages of reports from hundreds of sites to develop a high-quality, reliable dataset of remediation projects that targeted chlorinated solvents in groundwater. The efforts resulted in the accumulation of data from 235 remediation projects and 45 natural attenuation projects. Note that the terms "site" and "project" are used somewhat interchangeably to describe the results in this section; however, some sites (i.e., the geographical location) had multiple remediation efforts (i.e., projects) that targeted different areas within the site or different groundwater-bearing units. Such instances have been categorized as unique projects in the database even though they were conducted at the same site.

The following is a breakdown of some "database by the numbers" stats:

- 280 chlorinated solvent groundwater sites
  - ***235 in-situ remediation sites***
    - ⇨ 117 bioremediation sites
    - ⇨ 70 chemical oxidation sites
    - ⇨ 23 thermal treatment sites
    - ⇨ 21 chemical reduction sites
    - ⇨ 4 surfactant flushing sites
      - ⇔ 14 technology combination or "treatment train" sites
  - 45 natural attenuation sites
- 795 groundwater monitoring wells
  - ***710 wells at in-situ remediation sites***
  - 85 wells at natural attenuation sites
- 48,594 CVOC concentration data points
- An estimated 11,965 times that a well was sampled to collect the data in the database
  - Assuming that a well costs about $1,000 to sample (including labor, equipment, lab analyses, etc.), the approximate cost expended simply to collect the concentration data in our database was about $12 million. Of course the cost expended to implement the remediation projects was a significant multiple of this number.

Most of the projects in the database were located in the United States (see map below), with 1 site located in each of the following countries: Belgium, Canada, Czech Republic, Germany, and the United Kingdom.



Location Map of In-Situ Remediation Projects in the United States

4.2 Why Order of Magnitude?

An **Order of Magnitude (OoM)** is a factor of 10 change in a variable. For example, if a remediation technology reduces the dissolved phase concentration of TCE by one OoM, then the concentration is 10 times lower, equivalent to a 90% reduction. Two OoMs thus represents a reduction in concentration of 99%. The concept of OoMs is an important short hand for evaluating remediation performance because chlorinated solvent concentrations in groundwater typically span several orders of magnitude (Sale and Newell 2011), and are generally represented best by a log-normal statistical distribution.:

- 0 OoM: no change in concentration
- 1 OoM: 90% reduction in concentration
- 2 OoM: 99% reduction in concentration
- 3 OoM: 99.9% reduction in concentration

Hadley and Newell (2012) described how many groundwater-related variables are inherently Order of Magnitude processes and why groundwater remediation can best be considered "an Order of Magnitude endeavor":

> *"The OoM approach is useful because much of the environmental data associated with groundwater remediation is expressed in factors of 10, such as:*
>
> - *Hydraulic conductivity (for example, a sand, might be ''10^{-3} cm/s,'' while a clay might be ''10^{-6} cm/s''). Some groundwater professionals describe the hydraulic conductivity of a water-bearing unit as a ''10 to the minus 3 unit'' or ''10 to the minus 6 unit.'' This is an example of an OoM approach (powers of 10) being used to describe a key variable, hydraulic conductivity.*
> - *Concentration of VOCs is often expressed in powers of 10. For example, many concentration isocontour maps show power of 10 isocontours, such as 1 µg/L, 10 µg/L, 100 µg/L, 1000 µg/L, and 10,000 µg/L.*
> - *Mass discharge of contaminant plumes: One study showed a range of mass discharge measurements from contaminant plumes ranging from 0.00078 g/d to 56,000 g/d, or a range of 71 million (almost 8 OoMs). This is not surprising as mass discharge is the product of hydraulic conductivity and concentration data, both of which span many powers of 10.*
> - *Carcinogenic risk is commonly presented in OoMs: U.S. EPA's allowable risk ranges from 10^{-6} to 10^{-4} — another important factor expressed in orders of magnitude.*
> - *Remediation projects and decision tools are beginning to apply OoM concepts to management of groundwater plumes. For example, a Frequently Asked Questions document for DNAPLs proposed a ''rule of thumb'' (Sale et al. 2008) that indicated the typical reduction in concentration in groundwater achieved by chlorinated solvent remediation projects was ''one to possibly two'' OoMs. A landmark study of thermal remediation performance data used OoMs to report remediation performance at 14 well-studied thermal projects (Kingston et al. 2010).*
> - *OoMs are a key aspect when using the 14-Compartment Model for developing site conceptual models and developing remediation strategies (Sale and Newell 2011). OoMs are used to visualize what remediation can do at different media (vapor, DNAPL, aqueous, sorbed) and different locations at a site (source vs. plume)."*

The superiority of OoMs over a linear model for remediation performance can be seen in the following conceptual model about remediation. If a remediation project reduces the key groundwater metric (typically the maximum concentration at a site) from 5 mg/L to 0.5 mg/L, a linear model would suggest that this project has achieved a 90% reduction and that remediation goals could be achieved for only an additional 10% of the effort. The OoM approach would say that 1 OoM has been achieved, but two more OoMs are required to reach the cleanup standard,

and that 100% of the effort required to achieve the 1 OoM must be expended 2 more times in order to achieve the remediation goal (assuming the goal was to reach a 0.005 mg/L MCL).

Newell et al., 2011 used Order of Magnitudes to develop a plume classification system based on mass discharge. In their inventory of 40 sites, a nine order of magnitude difference between the largest mass discharge site (56,000 grams per day) and the smallest mass discharge site (0.00078 grams per day). Interestingly, the smallest site (0.00078 grams per day) was remediated using a thermal technology. But the key point is that removing 90% of the mass or reducing groundwater concentrations by 90% does not mean that 90% of the work has been done; because of the log-normal nature of contaminant transport and remediation processes, an Order of Magnitude model is much more appropriate for estimating remediation level of effort.

In the following sections of this ESTCP report, OoMs are used in a specific way: **to describe the reduction in groundwater concentrations from before to after an in-situ remediation project at an actual site. Different types of groundwater concentrations and calculation approaches are used, but all are reported as OoMs of reduction.**

4.3 Key Questions and Explanation of Graphics

The results of our project are presented in the following sections in the form of key questions that we believe are central to advancing the understanding of how well in-situ remediation technologies have performed (and how much they cost), and how these results might be useful for framing expectations of future or on-going remediation projects.

Much of the remediation performance results presented in the following sections are presented on graphs that we have termed “triangle charts.” Data points plotted on the X-axis of the chart represent concentrations before treatment began (or the first year monitoring concentration for MNA sites). Data points plotted on the Y-axis of the chart represent concentrations after treatment ended (or the last year monitoring concentration for MNA sites). Thus each data point on the chart represents actual before and after concentrations for an individual project.

From the location where the data point falls on the chart, the diagonal lines can be used to determine the OoM reduction achieved by the project based on the before and after treatment concentrations. The blue line toward the bottom of the chart represents the typical MCL of 0.005 mg/L for TCE and PCE, and can be used to determine whether a project achieved the MCL after treatment.

As discussed in Section 2 of this report, most of the concentrations presented in the following sections are geometric means, but occasionally maximum concentrations are presented for comparison. Beneath most charts we have included discussion of the “Data Shown” and an “Explanation” to reiterate what types of concentration data are being presented and help clarify the presentation of the data. Key Points are then provided to summarize the findings and answer the Key Question that was being asked.

4.4 What Performance Has Been Achieved at In-Situ Remediation Projects?

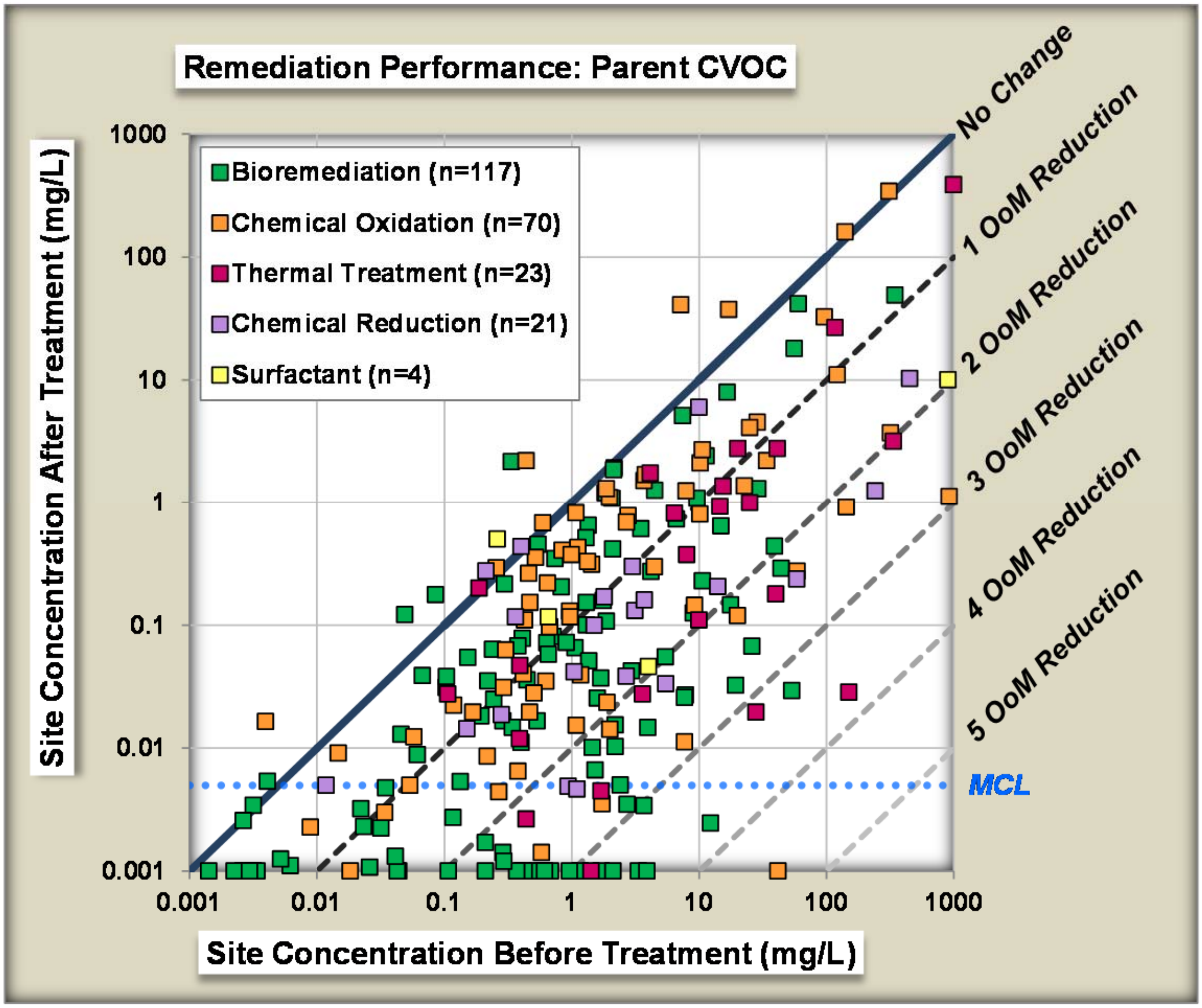


Figure 4.1. Remediation Performance of 235 In-Situ CVOC Remediation Projects.

Data Shown: *Geometric means of parent compound (for sites with multiple wells, the plotted value is the median of the geometric means from individual wells).*

Explanation: *Each symbol is an individual in-situ remediation project. The geometric mean treatment concentration from before treatment is shown on the X-axis, and the geometric mean treatment concentration from after treatment is shown on the Y-axis*

Key Points:

- Geometric means are shown, representing the typical before- and after-treatment concentrations from within the treatment zone.
- Parent concentrations are shown, representing mostly PCE sites, TCE sites with little or no PCE; and 1,1,1-TCA sites.

- Five remediation technologies are represented: 117 bioremediation projects; 70 chemical oxidation projects; 23 thermal remediation projects; 21 chemical reduction projects, and 4 surfactant projects.
- The performance of in-situ CVOC remediation performance technologies vary widely, from increasing by about 1 OoM to more than 4 OoM reduction in concentration.
- The middle 50% of the remediation projects achieved between 0.5 and 2 OoMs reduction in the geometric mean of the parent compound (between 71% and 99% reduction), with the median reduction at about **1.1 OoM (91% reduction).** Additional percentile results are summarized on Table 4.1 below.

Table 4.1. Order of Magnitude Reductions from 235 Active In-Situ Remediation Projects

Percentile of 235 Active In-Situ Remediation Projects	% Reduction in Geomean of Parent Compound in Treatment Zone	OoM Reduction in Geomean of Parent Compound in Treatment Zone
90%	99.8%	2.7
75%	98.9%	2.0
50%	91.2%	**1.1**
25%	71.4%	0.5
10%	30.8%	0.2

4.5 Does the Concentration Metric Matter? Geomeans vs. Maximums?

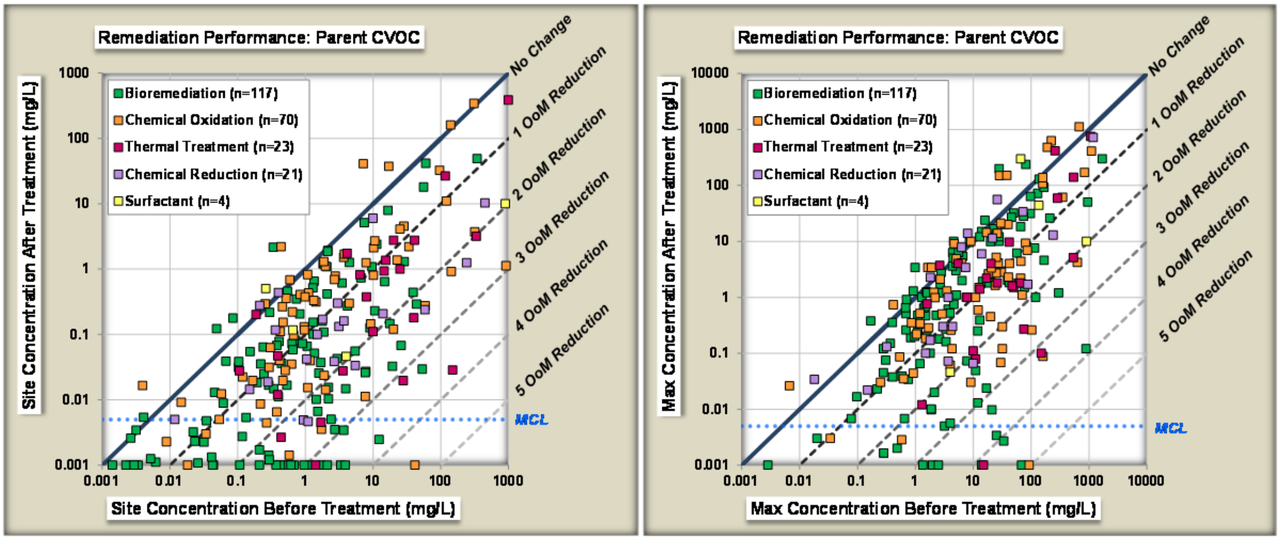


Figure 4.2a. Remediation Performance Based on Geometric Mean and Site Maximum Concentrations of Parent CVOC

Data Shown: *<u>Geomean</u> before and after concentrations of parent compound in treatment zone groundwater (left panel) and <u>Maximum</u> before and after concentrations of parent compound in treatment zone groundwater (right panel).*

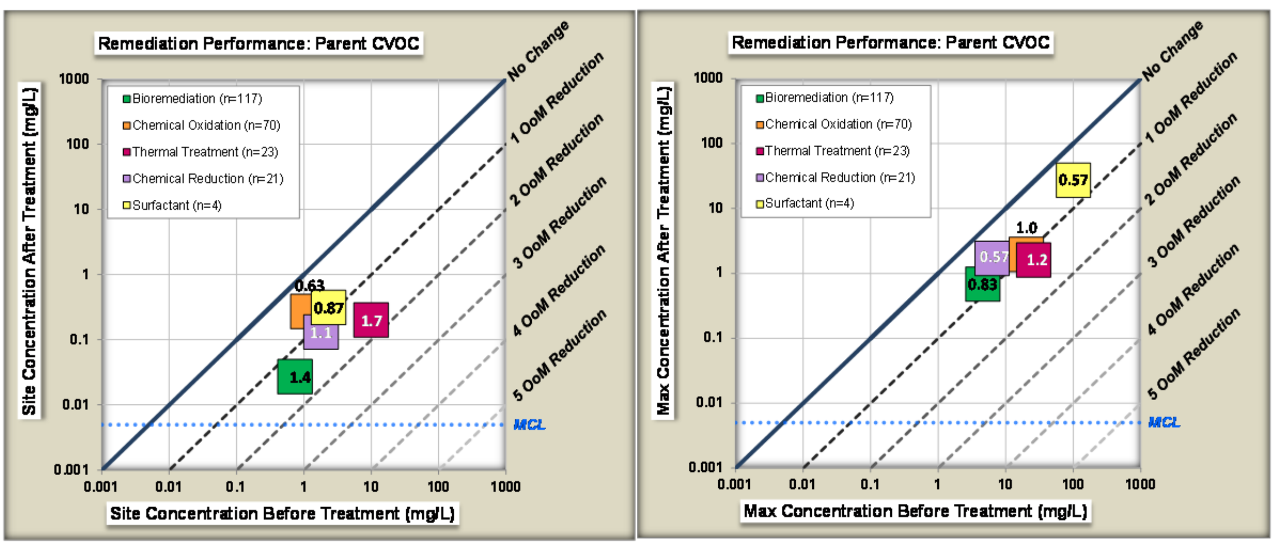


Figure 4.2b. Remediation Performance Based on Geometric Mean and Site Maximum Concentrations of Parent CVOC

Data Shown: *Median <u>geomean</u> before and after concentrations of parent compound (left panel) and median <u>maximum</u> before and after concentrations (right panel)*

Explanation: *The colored boxes show the median before and after concentrations for each technology. The numbers inside each box are the median OoM reduction. For example, the bioremediation projects had a median reduction in parent compound*

concentrations of 1.4 OoMs (96%) when using geomeans as the performance metric versus 0.83 OoMs (85%) when using maximum concentrations as the performance metric.

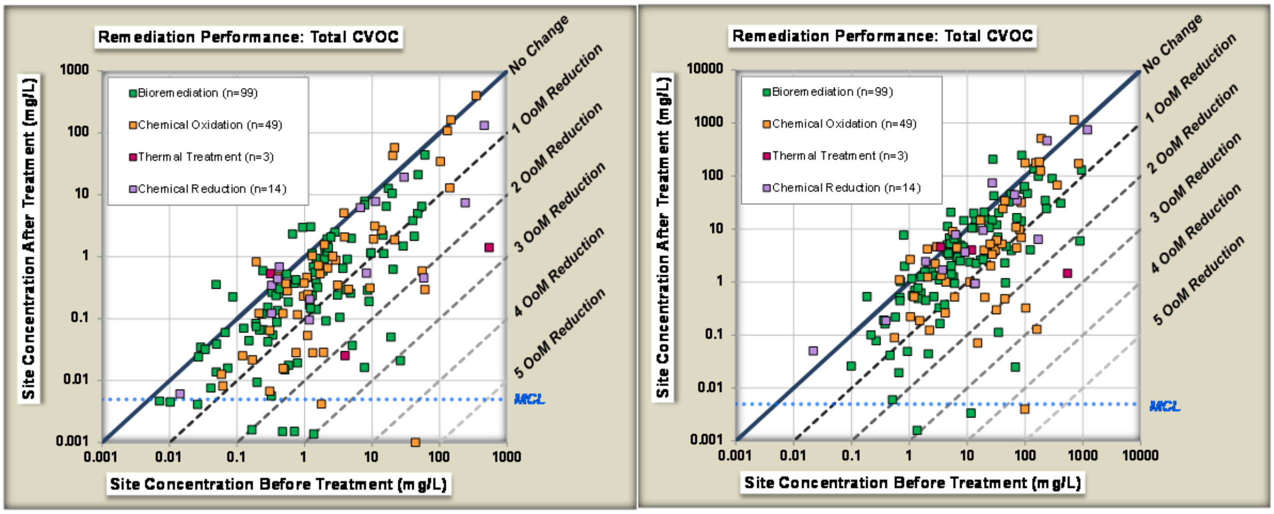


Figure 4.2c. Remediation Performance Based on Geometric Mean and Site Maximum Concentrations of Total CVOCs

Data Shown: *Geomean before and after concentrations of Total CVOCs in treatment zone groundwater (left panel) and Maximum before and after concentrations of Total CVOCs in treatment zone groundwater (right panel).*

Table 4.2. Order of Magnitude (OoM) Reduction in Parent Compound at 235 Remediation Sites Using Change in Geometric Means vs. Change in Maximum Concentrations

Percentile of 235 Sites	OoM Reduction (% Reduction) in Parent Geomean Concentration	OoM Reduction (% Reduction) in Parent Maximum Concentration
75th	2.0 (99%)	1.4 (96%)
50th	**1.1 (91%)**	**0.8 (84%)**
25th	0.5 (71%)	0.2 (41%)

Key Points:

- Remediation performance is generally poorer when site maximums are used as the performance metric (right panels) compared to geomeans (left panels). The exception was chemical oxidation, which showed better performance when using maximums (median OoM reduction of 1.0 using maximums vs. 0.63 using geomeans).

- When using site maximums, the middle 50% of all remediation projects achieved between **0.2 and 1.4 OoMs** reduction in the site maximum concentration of the parent compound (between 41% and 96% reduction), with the median reduction at about 0.8 OoM (84% reduction). By comparison, when using geomeans for evaluating performance, the middle 50% range of all projects was **0.5 to 2 OoMs** (between 71% and 99% reduction), with a median of 1.1 OoMs (91% reduction) (see Table 4.2).
- Using site maximums as the remediation performance metric appeared to reduce the performance of enhanced bioremediation, thermal, and chemical reduction projects by about 0.5 to 0.6 OoMs.
- One of the members of the Expert Review Panel, Dr. John Wilson, said that the **designers of a remediation project** would be more interested in geomeans, as this metric better represents performance throughout the treatment zone (see Appendix A).
- Dr. Wilson went on to say that **environmental regulators** are likely to be more interested in site maximum concentrations as a more relevant performance metric to determine whether regulatory cleanup standards can be achieved.
- Regulatory programs do not typically allow averaging or lumping of data from individual wells, making the site maximum concentration after treatment a key regulatory metric.

4.6 Does Performance Vary Significantly Between Technologies?

4.6.1 Is There a Difference in the Performance Data for the Four Major Technologies?

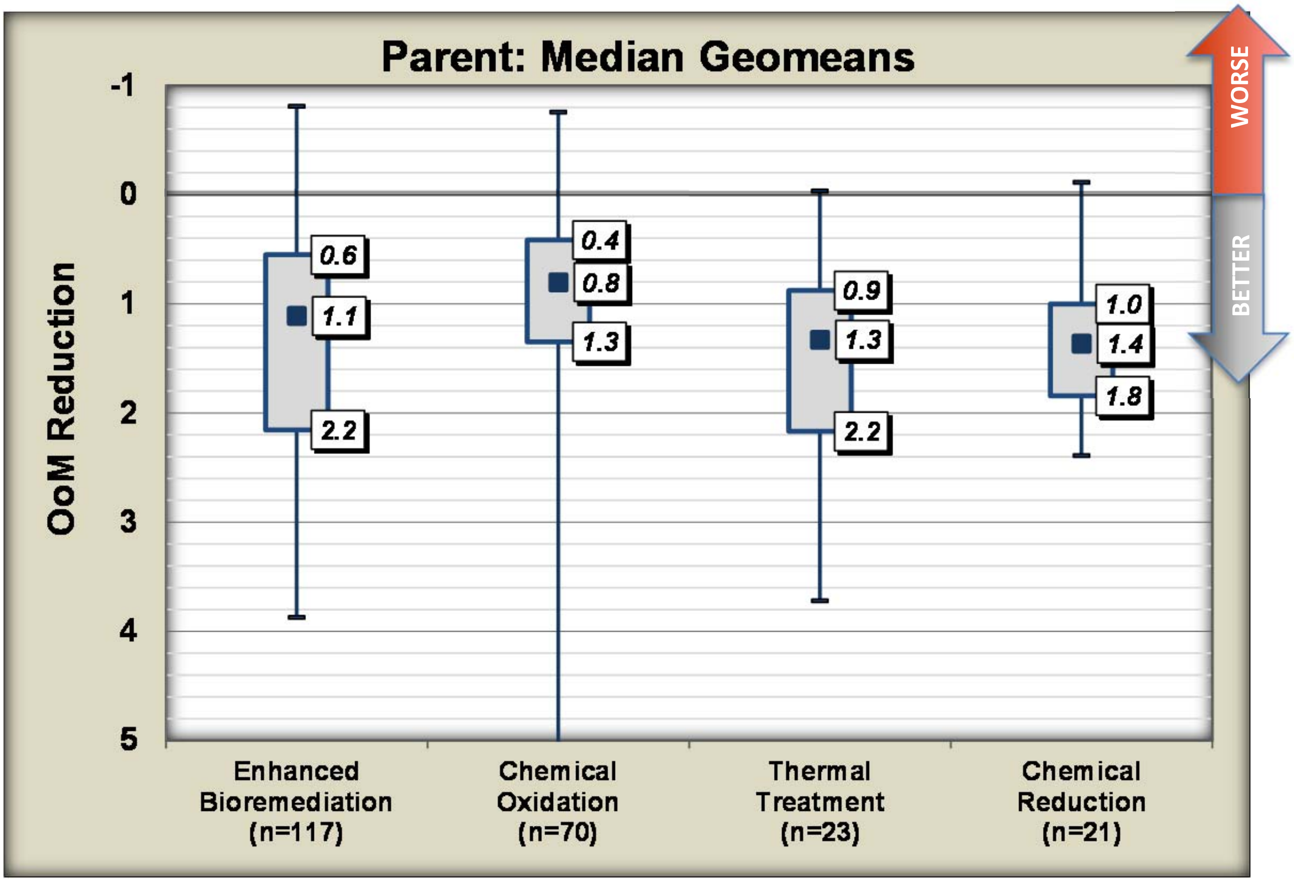


Figure 4.3. Groundwater Remediation Performance by Technology Based on Geomeans

Data Shown: *Change in geomean of parent compound concentrations in treatment zone groundwater by four different in-situ technologies.*

Explanation: *The grey boxes and upper and lower numbers show the 75th percentile and 25th percentile range (the middle 50%) of OoM Reduction for each technology. The black box and middle number are the median value. The upper and lower "whiskers" represent the maximum and minimum values.*

Key Points:

- When considering *geomean* concentrations for the *parent* compound, there does not appear to be significant differences in the performance of the four main technologies.
- Chemical oxidation appeared to have the worst performance (lowest OoM reduction) and thermal the best, but this is not statistically significant (see Section 4.6.3).
- But these conclusions change if a different metric is applied, such as the reduction in Total CVOCs (parents + daughter compounds + other CVOCs).

- Thermal treatment has been considered by some to have much better performance than other in-situ remediation technologies. However, practitioners often cite high performing *unsaturated soil* treatment projects to support this claim. This ESTCP project has focused exclusively on the change in **saturated zone groundwater concentrations** as measured in treatment zone monitoring points, and with the metric of *OoM reduction of parent compound concentrations in groundwater* thermal remediation performance is similar to the other technologies.
- Thermal remediation projects did appear to be applied at higher concentration sites (median before treatment concentration of 10 mg/L for the parent compound) and bioremediation has been applied at lower concentration sites (median before treatment concentration of 0.74 mg/L) (see Figure 4.4 and Table 4.2).

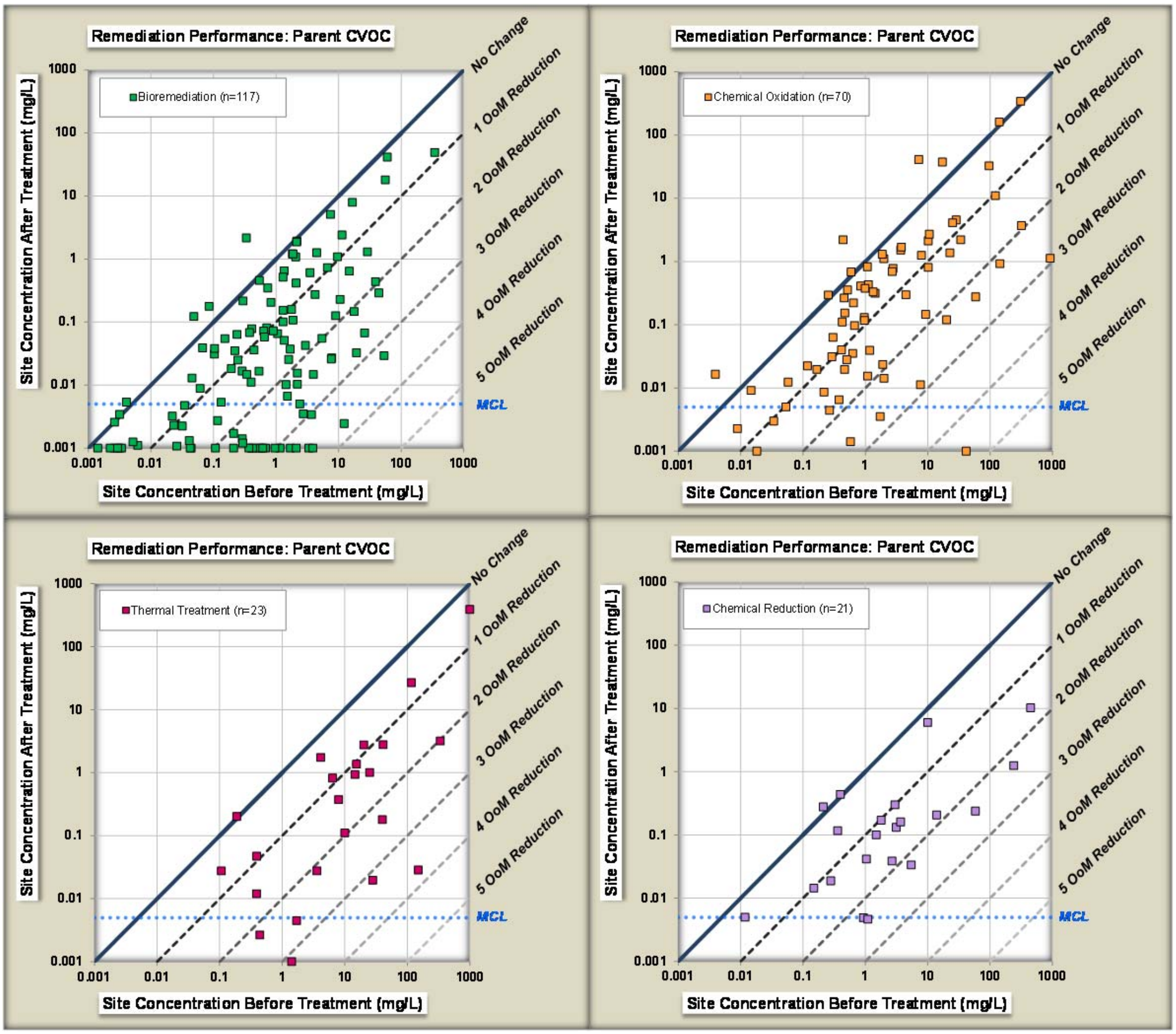


Figure 4.4. Remediation Performance by Remediation Technology

Data Shown: *<u>Geomean</u> concentration of parent compound*

Table 4.3. Before- and After-Treatment Groundwater Concentrations based on Geometric Means by Technology.

	Parent Median Geomean Before (mg/L)	Parent Median Geomean After (mg/L)	% Reduction in Parent Concentration	OoM Reduction in Parent Concentration*
Bioremediation (n=117)	0.74	0.027	96%	**1.4**
Chemical Oxidation (n=70)	1.1	0.27	77%	**0.6**
Thermal Treatment (n=23)	10	0.20	98%	**1.7**
Chemical Reduction (n=21)	1.8	0.13	93%	**1.1**

* Note the slight differences in median OoM Reduction values on this table and Figure 4.3 result from the order in which the negative log is applied to the before and after concentration data. For Figure 4.3, the negative log of individual projects was calculated first, then the median value was calculated for presentation on the chart. In this table the median concentrations of individual projects was first calculated, then the negative log of the medians was calculated.

4.6.2 Does the Technology Variation Matter?

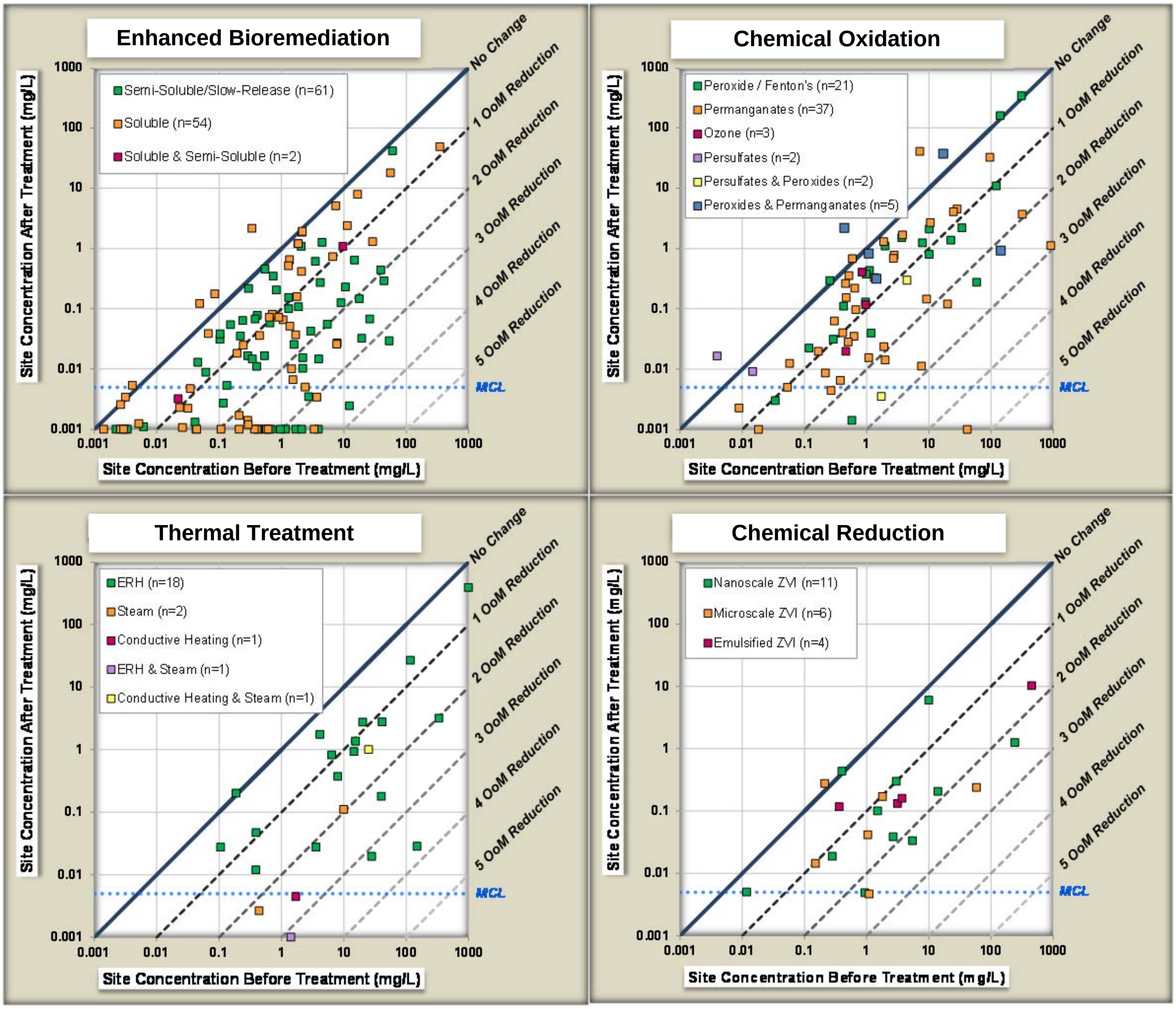


Figure 4.5. Change in *Geomean* Parent Compound Concentration by Technology Variant

Data Shown: *Change in* <u>*geomean*</u> *concentrations of* <u>*parent*</u> *compound for the different variations of the four technologies.*

Explanation: *Each symbol is an individual in-situ remediation project. The geometric mean treatment zone before concentration is shown on the X-axis, and the geomean after treatment concentration is shown on the Y-axis. The different colored symbols represent a different technology variation or "subtype" for each of the four main technologies.*

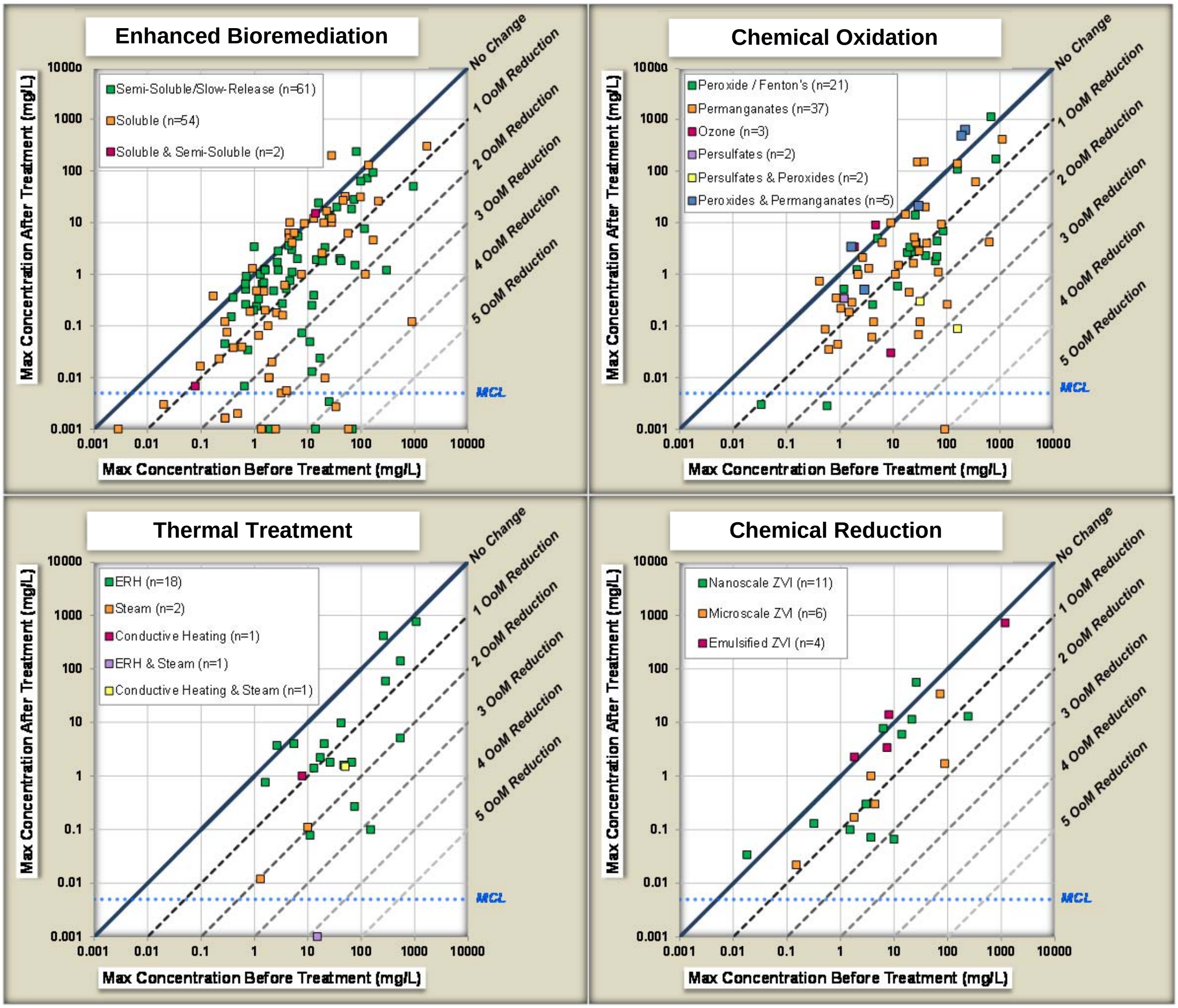


Figure 4.6. **Change in *Maximum* Parent Compound Concentration by Technology Variant**

Data Shown: *Change in <u>maximum</u> concentrations of <u>parent</u> compound for the different variations of the four technologies.*

Explanation: *Each symbol is an individual in-situ remediation project. The maximum treatment zone before treatment concentration is shown on the X-axis, and the maximum after treatment concentration is shown on the Y-axis. The different colored symbols represent a different technology variation or "subtype" for each of the four main technologies.*

Key Points

- While four major remediation technologies were evaluated (bioremediation, chemical oxidation, thermal remediation, and chemical reduction), each of these technologies has several variations "subtypes." For example, bioremediation was divided into "semi-

soluble/slow release" substrate projects (e.g., bioremediation using pure or emulsified vegetable oils), "soluble" substrate projects (e.g., bioremediation using lactate, molasses, or whey), and projects using a combination of both (e.g., a combination of oils and lactate).

- For bioremediation, projects were split fairly evenly between semi-soluble / slow release (n=61) and soluble substrates (n=54), with only 2 sites reporting a combination of both types of substrates. Interestingly, only 7 bioremediation projects reported bioaugmentation as part of the remedial strategy. Due to the low number of bioaugmentation projects, these were not evaluated for performance against non-bioaugmented projects.
- For chemical oxidation, peroxide / Fenton's reagent and permanganates dominated with a total of 58 of the 70 projects. Less commonly applied chemical oxidation amendments included ozone (n=3), persulfates (n=2), or a combination of persulfates and peroxides (n=2) or a combination of peroxides and permanganates (n=5).
- For thermal treatment, electrical resistance heating (ERH) projects had the largest representation with 18 of the 23 projects. Steam was implemented at 2 sites, while conductive heating and combinations of ERH & steam or conductive heating & steam were reported at 1 site each. The low number of conductive heating sites appears to be due to the general lack of groundwater monitoring as a performance metric for these projects. Instead, vendors typically rely on soil samples from before and after treatment. While this may be a reasonable project or technology-specific approach, regulatory decisions concerning groundwater restoration and ultimate site closure nearly always depend on groundwater concentrations. It is for this reason that our project relied upon groundwater concentrations for performance assessment, and therefore precluded the use of project with soils only data.
- No significant differences were observed for the different technology variations.

4.6.3 Were the Performance Results for Any Technology Statistically Different than the Other Technologies?

Table 4.4. Statistical Comparison of Remediation Performance by Technology

Geomean of Parent OoM Reductions				
Tech Comparison	**Chem Ox.**	**Thermal**	**Chem Red.**	**All Others**
Bioremediation (Bio) (n=117)	YES Bio>CO 1.1 > 0.8 (p=.0095)	No - - (p=0.43)	No - - (p=0.995)	No - - (p=0.11)
Chemical Oxidation (CO) (n=70)	-	YES Therm>CO 1.3 > 0.8 (p=0.012)	No - - (p=0.067)	YES Other>CO 1.2 > 0.8 (p=0.003)
Thermal (Therm) (n=23)	-	-	No - - (p=0.61)	No - - (p=0.14)
Chemical Reduction (CR) (n=21)	-	-	-	No - - (p=0.56)

Maximum of Parent OoM Reductions				
Tech Comparison	**Chem Ox.**	**Thermal**	**Chem Red.**	**All Others**
Bioremediation (Bio) (n=117)	No - - (p=0.82)	No - - (p=0.19)	No - - (p=.23)	No - - (p=0.925)
Chemical Oxidation (CO) (n=70)	-	No - - (p=0.15)	No - - (p=0.38)	No - - (p=0.75)
Thermal (Therm) (n=23)	-	-	No - - (p=0.054)	No - - (p=0.11)
Chemical Reduction (CR) (n=21)	-	-	-	No - - (p=0.20)

Geomean of Total CVOCs OoM Reductions				
Tech Comparison	**Chem Ox.**	**Thermal**	**Chem Red.**	**All Others**
Bioremediation (Bio) (n=99)	No - - (p=0.54)	No - - (p=0.37)	No - - (p=0.12)	No - - (p=0.91)
Chemical Oxidation (CO) (n=49)	-	No - - (p=0.39)	No - - (p=0.10)	No - - (p=0.43)
Thermal (Therm) (n=3)	-	-	No - - (p=0.43)	No - - (p=0.36)
Chemical Reduction (CR) (n=14)	-	-	-	No - - (p=0.10)

Maximum of Total CVOCs OoMs Reductions				
Tech Comparison	**Chem Ox.**	**Thermal**	**Chem Red.**	**All Others**
Bioremediation (Bio) (n=99)	No - - (p=0.13)	No - - (p=0.76)	No - - (p=0.071)	No - - (p=0.50)
Chemical Oxidation (CO) (n=49)	-	No - - (p=0.97)	YES CO>CR 0.7 >0.2 (p=.023)	No - - (p=0.071)
Thermal (Therm) (n=3)	-	-	No - - (p=0.35)	No - - (p=0.77)
Chemical Reduction (CR) (n=14)	-	-	-	YES Other>CR 0.4 >0.2 (p=.040)

Data Shown: *Outcome of a two-tailed Mann-Whitney Test at the 0.05 significance level between OoM Reductions of each technology's for the different metrics (i.e., geomeans vs maximums and parents vs. totals). The median of OoM Reduction of the two populations are also listed for the cases in which there was a statistical difference.*

Explanation: *Each table is distinguished by metric; each compares the technology pairs by performing a Mann-Whitney Test. The test results were listed as the probability value based upon the pair of data sets associated with a specific technology. Furthermore, each technology was also compared to the combined OoM Reductions of the three other technologies, which is designated by the "All Others" category. The Boolean listed ("Yes" or "No") serves to answer the question of statistical difference based on the p-value generated at a given significance level – for a p-value below the significance level, in this case 0.05, the null hypothesis that both populations have the same central distribution (which can be viewed as a comparison of two medians) is rejected. Correspondingly, if the p-value is greater than the given significance level, the null hypothesis cannot be rejected, indicating that there is no statistical evidence indicating that the two populations differ. If the results indicated a statistical difference, the median OoM reductions were shown to indicate which technology had a central distribution that was relatively greater than the other, which may indicate a better statistical performance.*

Key Points

- The Mann-Whitney Test (i.e., the Wilcoxon Rank Sum test) is a non-parametric test that compares the central distribution (median values) of two unpaired groups of according to the null hypothesis that they are not different. The Mann-Whitney Test was performed in this case because it has a higher efficiency than the t-test on non-normal distributions or mixtures of normal distributions. In this incidence, the data could not be assumed to all behave under a Gaussian distribution; thus, the Mann-Whitney Test was selected to be performed.
- While the higher median between populations has been included in the tables, it is important to note that we performed a two-tailed Mann-Whitney Test. Using a two-tailed test allots half of the statistical significance level to each tail of the distribution of the test statistic; as such, a two-tailed test investigates the possibility of the relationship occurring in both directions. At the 0.05 significance level, a two-tailed test indicates that the populations are statistically different only if the test statistic is calculated to be within the top 2.5% or the bottom 2.5% of the probability distribution, which would indicate a probability value less than the significance level of 0.05.
- There were only five instances at which the difference in central distribution between two populations differed enough to be considered statistically significant; interestingly, four out of the five instances involved chemical oxidation. Furthermore, among these four, three scenarios indicated that the median of chemical oxidation was less than the respective value for the comparative technology.
- Largely, most comparisons indicated that there is no significant evidence of differing central distributions in each pair of population, signifying an overall higher p-value than the significance level. In total, this confirms that the four major technologies generally achieve similar results.

4.7 Does Performance Change when using Total CVOCs vs. Parent Compounds?

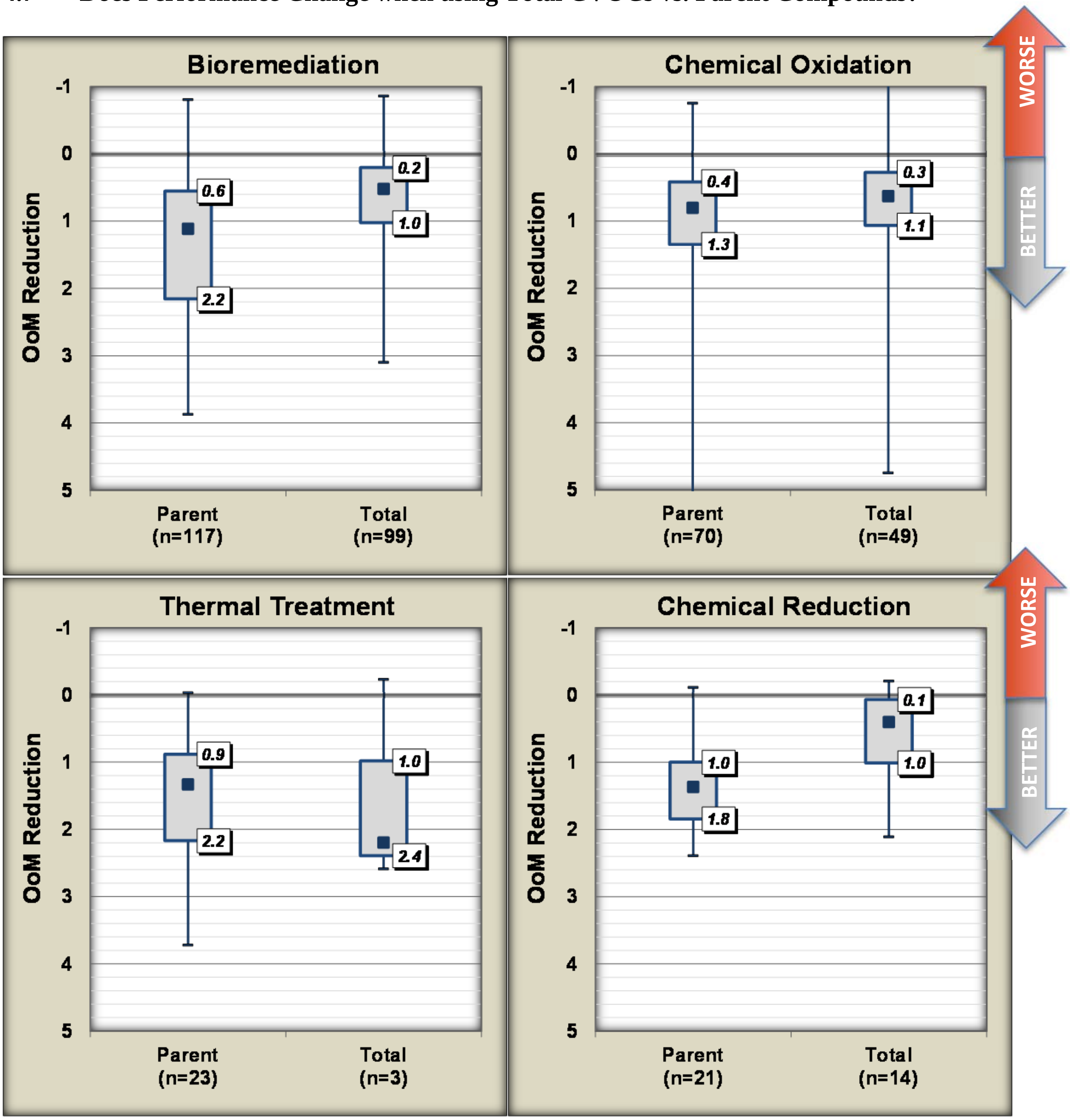


Figure 4.7. Comparison of Remediation Performance Based on Parent Compound (left whisker plot in each panel) and Total CVOC Concentration (right whisker plot in each panel).

Data Shown: *OoM reduction distribution based on geomean concentrations of Parent vs. Total CVOC concentration for bioremediation, chemical oxidation, thermal treatment, and chemical oxidation projects.*

Explanation: *The grey boxes and numbers show the 75th percentile and 25th percentile range (the middle 50%) of OoM reductions. The black box shows the median value. The "whiskers" show the maximum and minimum values.*

Key Points:

- The contaminant metric, in this case the Parent compound vs. Total CVOCs (i.e., parent plus daughter products), affects the performance of each remediation technology. Poorer performance was generally observed when the Total CVOC was the contaminant metric.
- Chemical oxidation projects were least impacted when *Total CVOC concentrations* were used compared to the *parent compound concentration. The median OoM reduction was only slightly smaller for Total CVOCs than parent compound concentrations, though this results is statistically significant (p=0.0003 based on Mann-Whitney test).* This pattern is expected as chemical oxidation does not result in the production of daughter products.
- Bioremediation and chemical reduction projects had worse performance when Total CVOCs is used as a metric compared to parent compound reductions ($p<0.05$ for both technologies based on Mann-Whitney test). This is also expected because enhanced bioremediation converts parent compounds to daughter products (note that chemical reduction has far less potential for the formation of daughter products, unless combined with a biological substrate), and both are generally less efficient at removing the lower chlorinated CVOCs.
- Thermal remediation projects also had worse performance for Total CVOCs; however, only 3 thermal projects had Total CVOC data. No statistical difference could be established.
- The question of which metric is more appropriate to use is a complicated one, as one commonly found non-parent compound (cis-1,2-DCE) has significantly lower risk than its parent compound, while 1,1-DCE, a degradation product of 1,1,1-TCA has higher risk. The natural attenuation potential for lower chlorinated compounds is generally higher than the parent compounds as aerobic biodegradation reactions can degrade several of the key daughter products (such as vinyl chloride). For this project most of the analysis focused on the reduction in the parent compounds, but the data in Figure 4.7 are shown for comparison purposes.
- Analysis of Total CVOCs was problematic due to inconsistent availability of daughter product concentrations among the data sources (and even within individual sites) and the high variability in detection limits and concentrations of the daughter products. For example, sites often had elevated detection limits for daughter products with sporadic detections at concentrations sometimes higher and sometimes lower than the detection limits reported in other samples collected from the same monitoring well. Therefore, only detected concentrations of daughter products were quantified in the database, which further reduced the data population available for evaluation of Total CVOCs. Another option would have been to quantify non-detects as the detection limit, or one-half the detection limit, but doing so would have likely resulted in an over-estimate of actual concentrations due to the often elevated detection limits. As such, the analysis of Total CVOC performance data and associated outcomes carry greater uncertainty than the results based on parent CVOC concentrations.

4.8 Do Other Factors Such as Chemicals, Geology, Project Size, and Depth Correlate to Remediation Performance?

4.8.1 Does the Type of Parent Compound Matter?

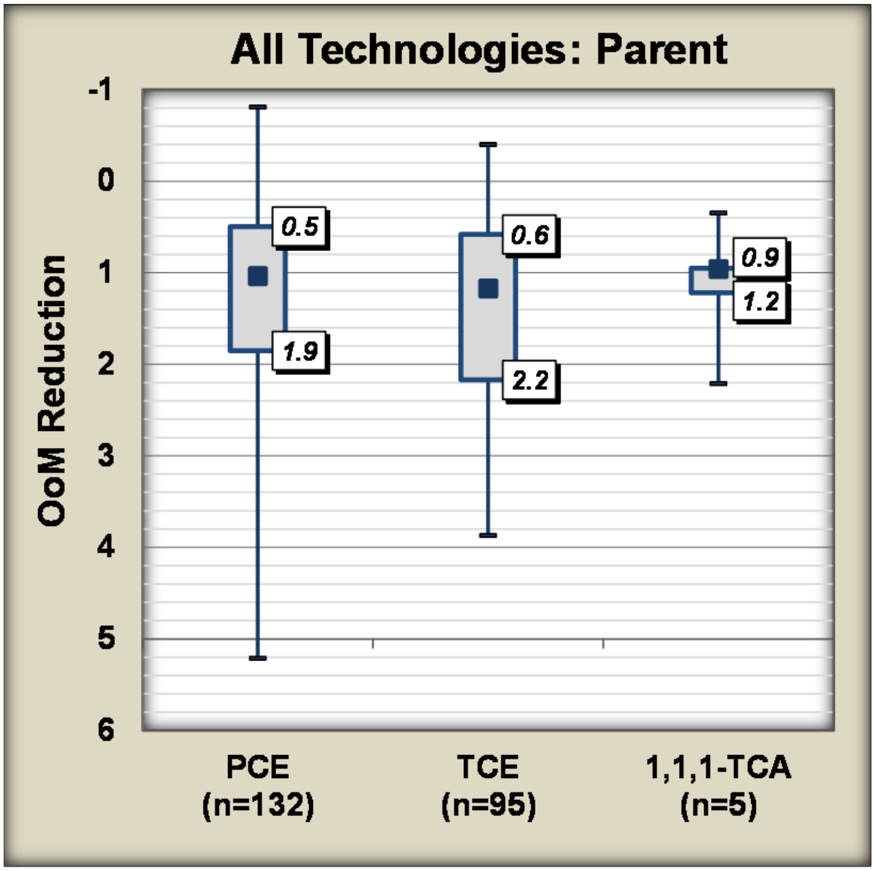


Figure 4.8. Remediation Performance Based on Parent Compound.

Data Shown: *Distribution of OoM Reductions based on geomean concentrations of parent compounds in treatment zone for sites with either PCE, TCE, or 1,1,1-TCA, as the predominate parent compound.*

Explanation: *The grey boxes and numbers show the 75th percentile and 25th percentile range (the middle 50%) of OoM results for each category. The black box shows the median value. The "whiskers" show the maximum and minimum values.*

Key Points

- The type of parent compound has very different properties such as different solubility (approximately 143, 1100, and 1260 mg/l for PCE, TCE, and 1,1,1-TCA respectively) and different degradation reactions (PCE has an additional step for reductive dechlorination reactions; 1,1,1-TCA has an abiotic hydrolysis reaction); these factors did not seem to have a significantly effect on remediation performance.

- The performance for all in-situ remediation projects was similar for sites with PCE as the parent compound, TCE as the parent compound, and 1,1,1-TCA as the parent compound. When comparing the OoM reductions for the two most frequent parent CVOCs (PCE and TCE), no significant difference could be established (p=0.27 based on Mann-Whitney test).
- The same result of "no significant difference between parent compounds" was observed when the performance metric was the change in the parent compound and when the metric was Total CVOCs.
  - This implies that chemical factors may be secondary to other factors when considering remediation performance.
  - Some differences were seen by technology (Figure 4.9); the performance of chemical oxidation projects was significant better at TCE dominated sites compared to PCE dominated sites (p=0.02 based on Mann-Whitney test).

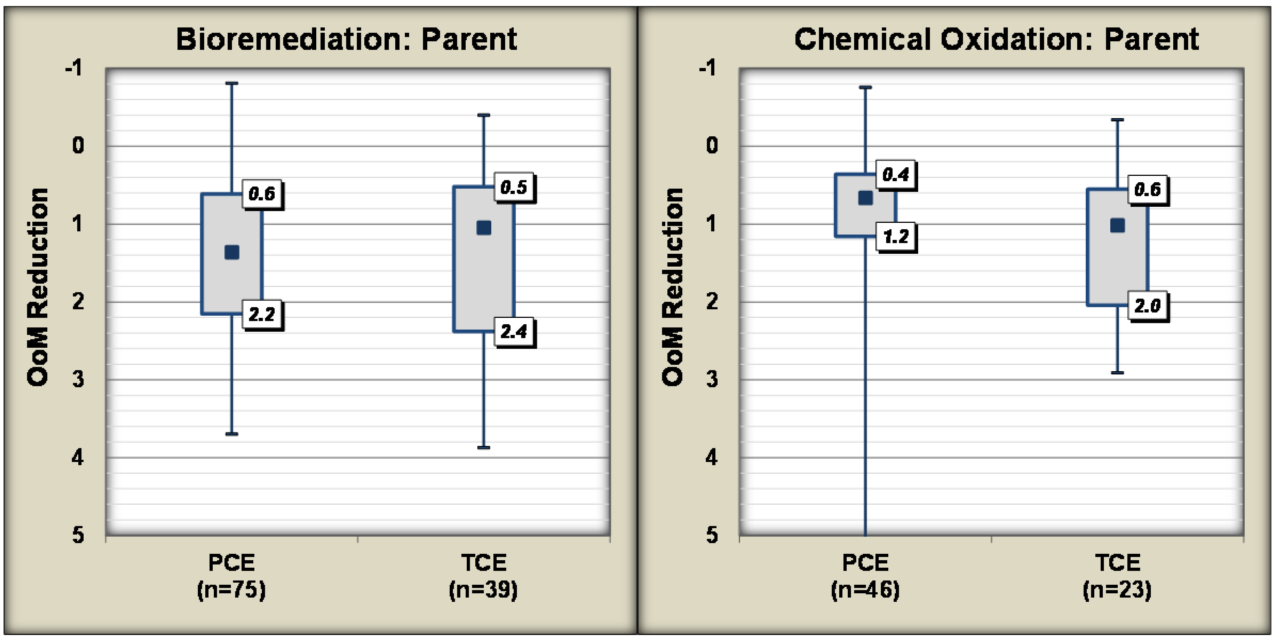


Figure 4.9. Comparison of Remediation Performance Based on Type of Parent Compound for Bioremediation Projects (left panel) vs. Chemical Oxidation Projects (right panel).

Data Shown: *Distribution of OoM Reductions based on geomean concentration of parent compounds for bioremediation (left panel) vs. chemical oxidation projects (right panel) for sites with PCE or TCE as the predominate parent compound.*

Explanation: *The grey boxes and numbers show the 75th percentile and 25th percentile range (the middle 50%) of OoM results for each category. The black box shows the median value. The "whiskers" show the maximum and minimum value*

4.8.2 Can the Effect of Geology Be Seen in the Remediation Performance Data?

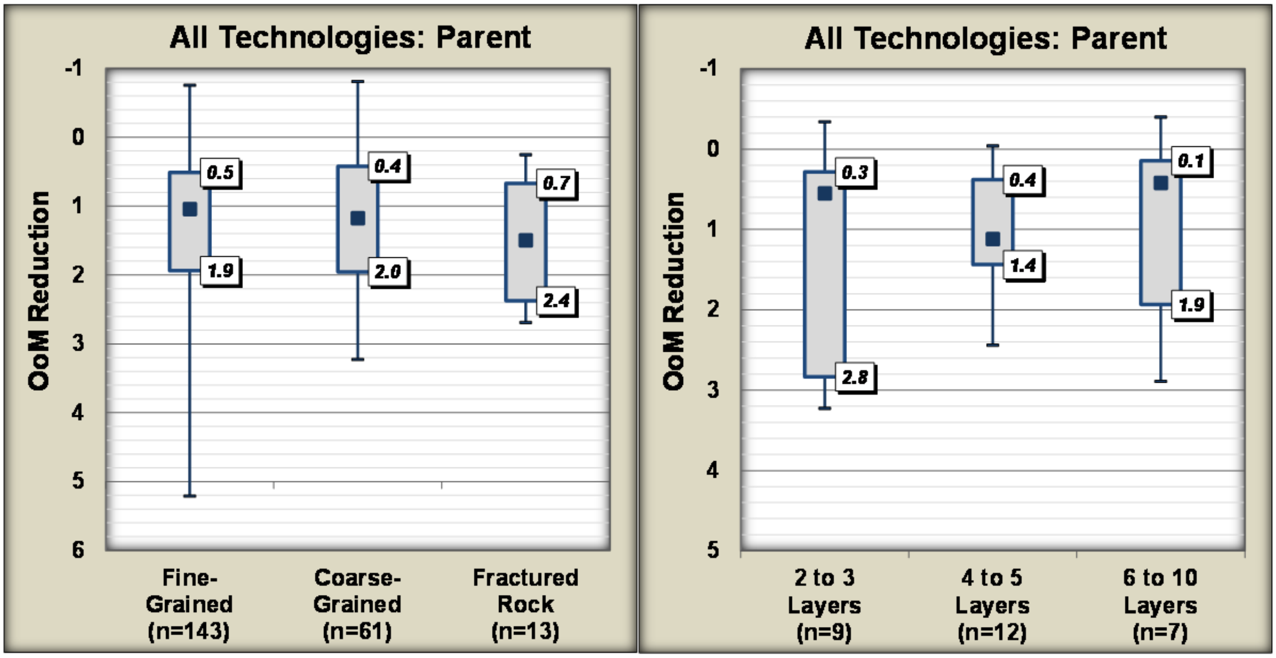


Figure 4.10. Comparison of Remediation Performance Based on Predominate Soil Type in Treatment Zone (left panel) and Number of Layers as Indicated in Treatment Zone Boring Logs (right panel).

Data Shown: *Distribution of OoM Reductions based on geomean concentration of parent compounds by predominate treatment zone soil type (left panel) and number of different stratigraphic layers as identified in treatment zone boring logs (right panel).*

Explanation: *The grey boxes and numbers show the 75th percentile and 25th percentile range (the middle 50%) of OoM results for each category. The black box shows the median value. The "whiskers" show the maximum and minimum value*

Key Points

- One well-accepted design rule for in-situ remediation projects is that treatment is easier (and performance supposedly better) for sites with more permeability and homogeneity, and that treatment of fractured rock sites is significantly more difficult than unconsolidated sites.
- However the performance data from this project did not see this effect; the overall performance of fine-grained sites *as defined by the available data* is comparable to coarse grained sites (p=0.96 based on Mann Whitney test).
- Surprisingly, the performance at 13 fractured rock sites was about 0.3 OoMs better than the unconsolidated sites, though this effect was not statistically significant (p=0.24).
- When considering the number of layers in the treatment zone (defined as the average number of distinct Universal Soil Classification System (USCS) layers in the vertical target zone

based on treatment zone borings), there did not seem to be consistent, significant differences between the sites.

- This may be because the commonly used USCS does not distinguish key stratigraphic features that impact remediation, and that high-resolution site characterization techniques such as pore-water pressure testing with direct push rigs, detailed grain size analysis, and more relevant soil classification systems such as the Udden-Wentworth classification system, are needed to “see” the impacts of heterogeneity on remediation performance.
- When the performance is evaluated on an individual well basis (Figure 4.11), no distinct relationship between the remediation performance (in terms of OoM Reduction) vs. number of layers is observed. It is speculated that the number of layers identified in this graph is more a function of attention to detail of the person doing the geologic logging (and potentially if the person logging the soil samples was a seasoned geologist vs. junior engineer!).

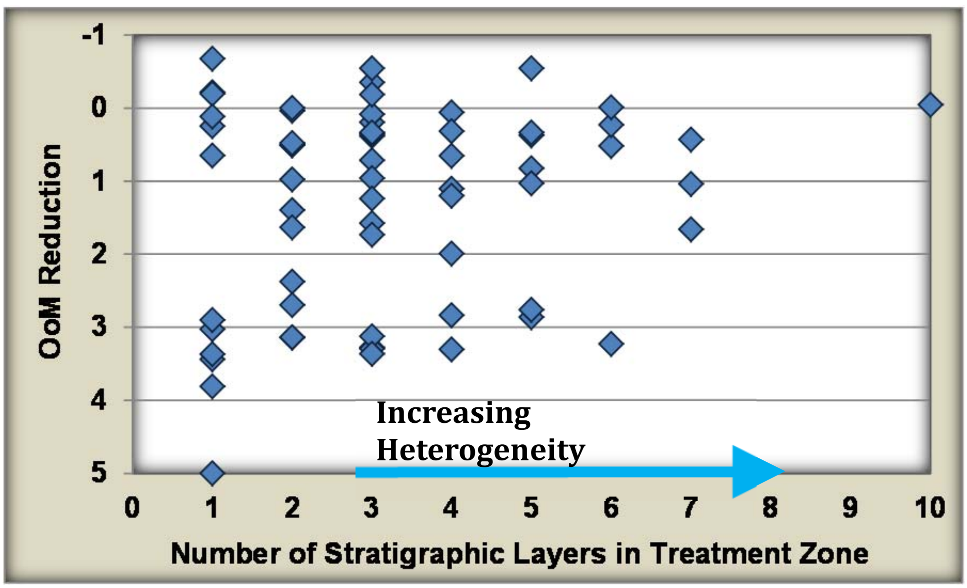


Figure 4.11. OoM Reductions for Parent Compounds vs. Number of Stratigraphic Layers in Treatment Zone From USCS

Data Shown: *Change in geomean concentration of parent compounds in individual wells in remediation treatment zone by number of stratigraphic layers indicated by Universal Soil Classification System (USCS)*

Explanation: *Each dot shows the change in concentration in terms of Order of Magnitude Reduction due to remediation. The X-Axis shows an increasing number of layers as indicated in the boring log for that well.*

4.8.3 *Does the Size, Scale, or Depth of Treatment Correlate to Remediation Performance?*

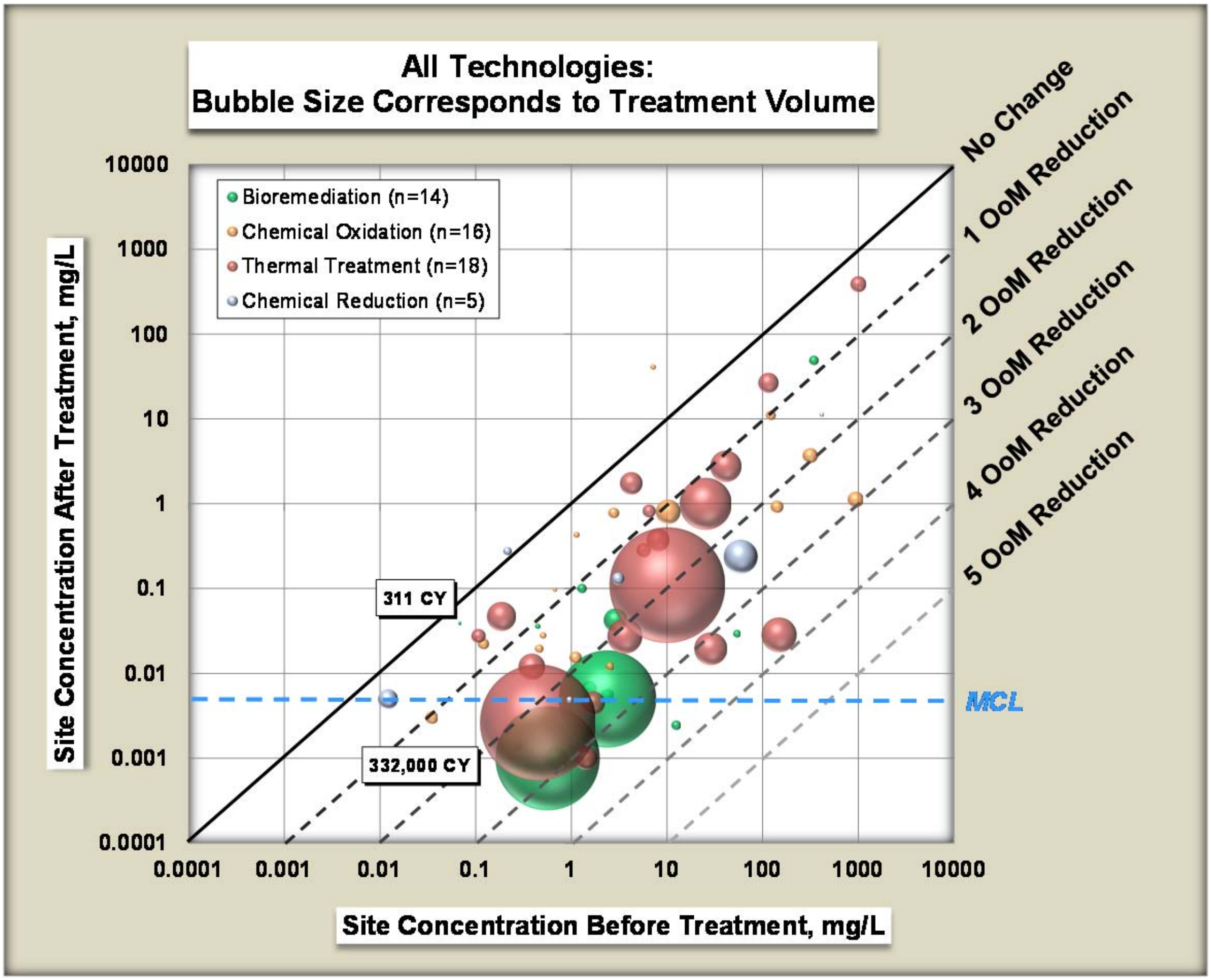


Figure 4.12. Treatment Zone Volume vs. Performance

Data Shown: *Geometric means of parent compound before treatment concentration on the X-axis and after treatment concentration on the y-axis.*

Explanation: *Each symbol is an individual in-situ remediation project. The size of the circle correlates to the treatment volume, which ranged from 311 (smallest circle) to 332,000 cubic yards (largest circle).*

Key Points

- Some remediation experts have hypothesized that larger in-situ remediation projects might exhibit better performance because it minimizes the chance for recontamination of the treatment zone from surrounding untreated areas.
- Based on the data compiled for this project, the four largest projects appeared to have better-than average performance (median performance of 2.5 OoMs vs. 1.1 OoMs for all 235 remediation projects).

- The median treatment volume for 54 projects with volume data was about 5,000 cubic yards. 90% of the in-situ remediation projects were 30,000 cubic yards or less (see Table 4.5).
- The depth of the treatment zone did not seem to correlate to remediation performance (see Figure 4.14). No statistically significant difference between the groups could be established (p=0.24 based on ANOVA). However, the data do suggest that slightly better performance was observed for projects with a treatment zone depth range of 21 to 40 feet (see Table 4.6).

Table 4.5. Distribution of Treatment Volume for 54 In-Situ Remediation Projects

Percentile of Treatment Projects	Treatment Volume (Cubic Yards)
Minimum	311
10%	793
25%	2,010
50%	**4,971**
75%	14,549
90%	30,000
Maximum	332,000

Table 4.6. Order of Magnitude (OoM) Reduction in Parent Compound at 151 Remediation Sites by Treatment Zone Depth

Percentile of 151 Sites	5 to 20 Ft. (n=39)	21 to 40 Ft. (n=64)	41 to 60 Ft. (n=31)	61+ Ft. (n=17)
75th	1.5	2.1	1.8	1.8
50th	**1.0**	**1.2**	**1.1**	**0.7**
25th	0.4	0.7	0.6	0.2

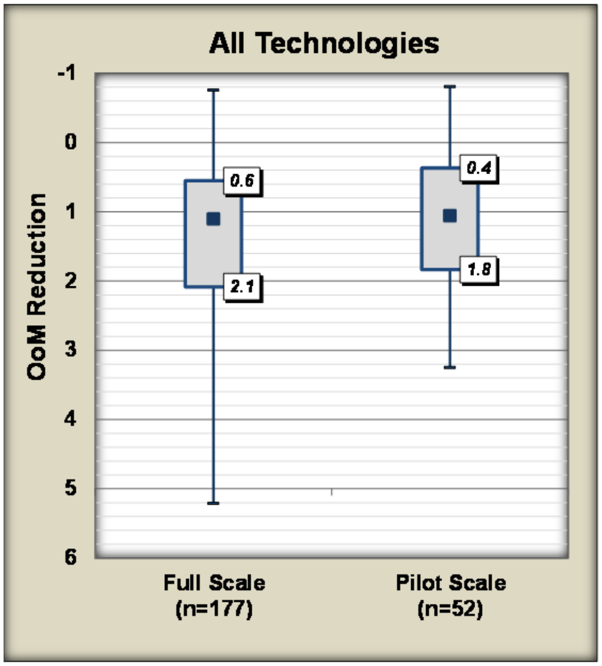


Figure 4.13. Performance for Full Scale vs. Pilot Scale Projects

Data Shown: *Distribution of OoM Reductions based on geometric mean concentrations of parent compound.*

Explanation: *The grey boxes and numbers show the 75th percentile and 25th percentile range (the middle 50%) of OoM reductions for each category. The black box shows the median value. The "whiskers" show the maximum and minimum value.*

Key Point

Only small differences (0.2 OoMs) were observed when 185 full-scale projects were compared to 52 self-described "Pilot Tests" (see Figure 4.13).

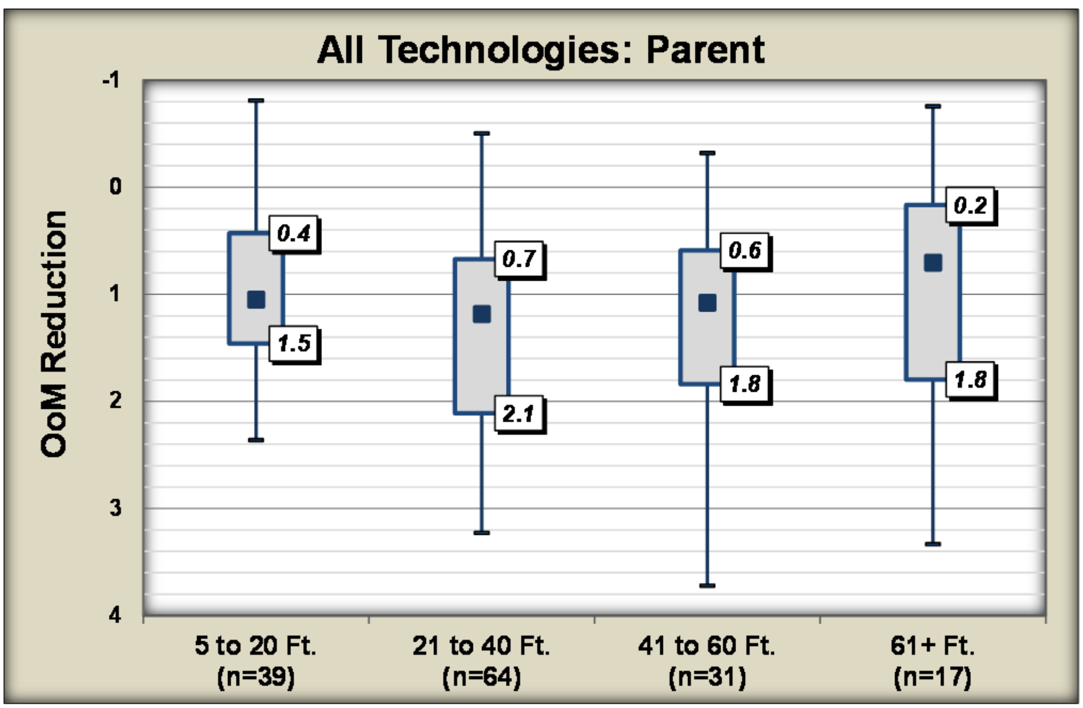


Figure 4.14. Depth of Treatment Project vs. Performance

Data Shown: *Distribution of OoM Reduction based on geometric means of parent compound.*

Explanation: *The grey boxes and numbers show the 75th percentile and 25th percentile range (the middle 50%) of OoM results for each category. The black box shows the median value. The "whiskers" show the maximum and minimum value.*

4.9 Does Treatment Duration, Monitoring Duration, or the Number of Monitoring Points Correlate to Performance?

4.9.1 Does Treatment Duration Matter?

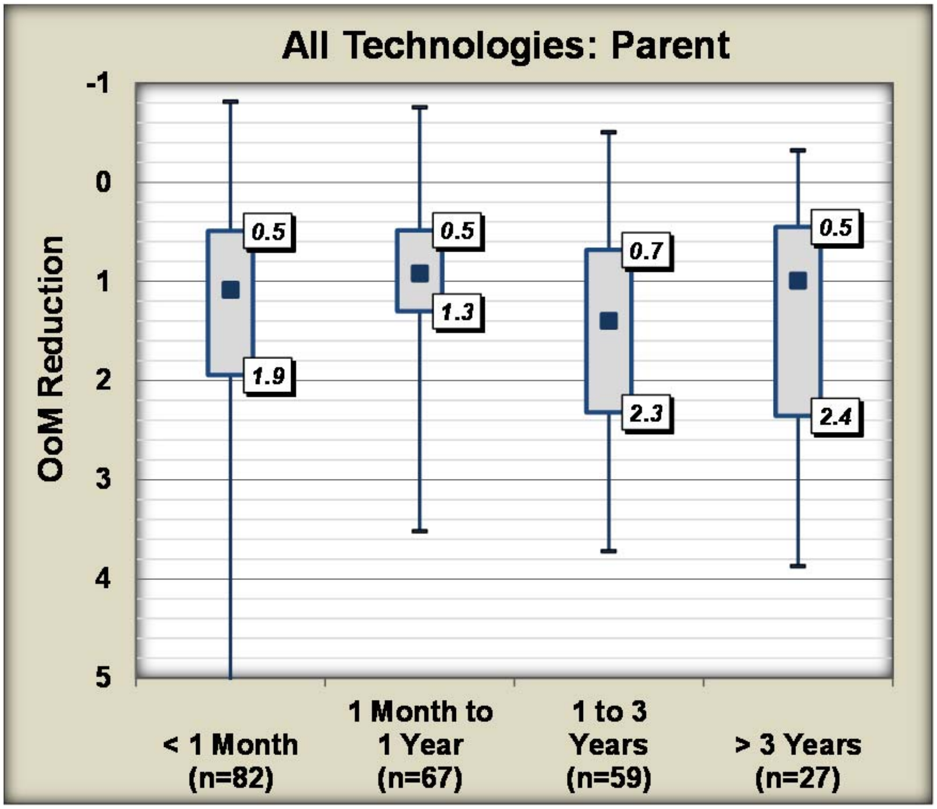


Figure 4.15. Treatment Duration vs. Performance

Data Shown: *Distribution of OoM Reduction based on geometric means of parent compound.*

Explanation: *The grey boxes and numbers show the 75th percentile and 25th percentile range (the middle 50%) of OoM results for each category. The black box shows the median value. The "whiskers" show the maximum and minimum value.*

Key Points

- Treatment duration is defined as the time between the *initial injection event, or startup* of a thermal project, to the *final injection event, or shutdown* of a thermal project. Treatment durations for the 235 projects ranged from <1 month (essentially a single injection event) to more than 13 years for 1 bioremediation project that consisted of a series of injection events over time. Only 8 sites had treatment durations exceeding 5 years. The middle 50% range of treatment durations was about 1 week to 1.7 years, with a median of 6 months.
- Performance was relatively consistent across the treatment durations reported for the 235 projects. However, projects with a treatment duration exceeding 1 year performed slightly better than those with less than 1 year of treatment duration (p=0.02 based on Mann-Whitney test).

4.9.2 Does Monitoring Duration Matter?

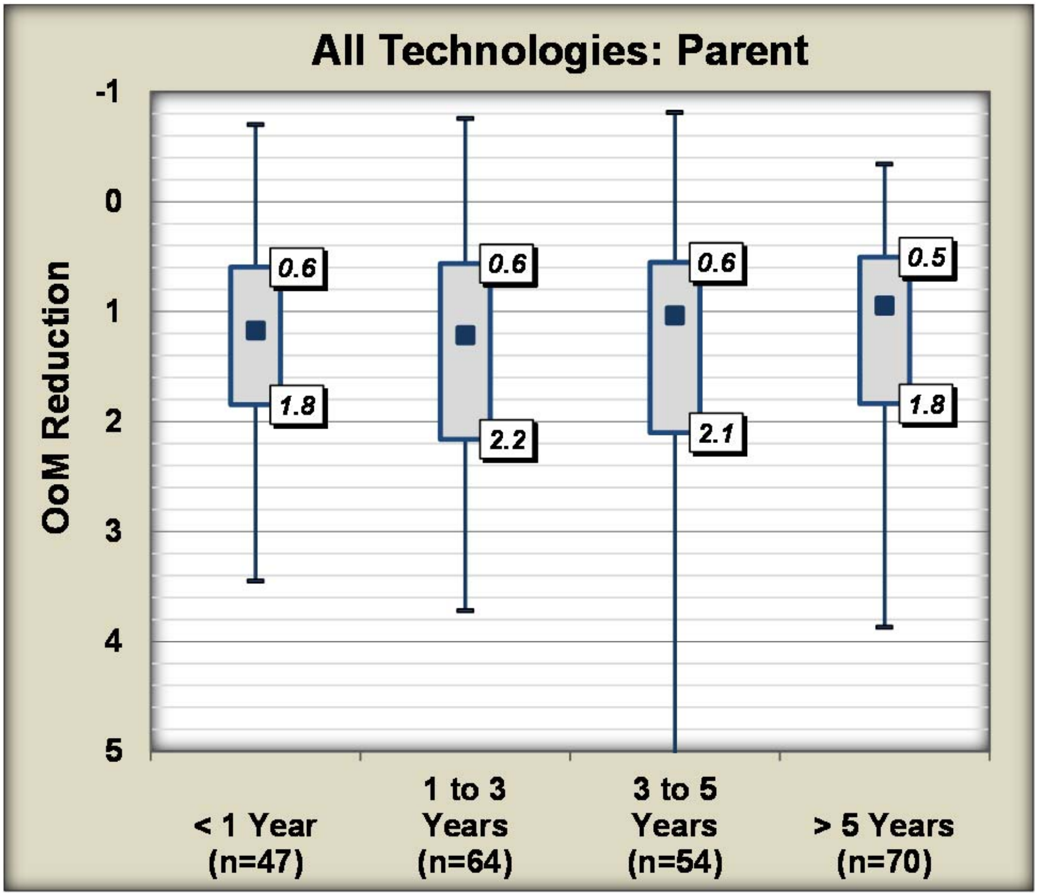


Figure 4.16. Monitoring Duration vs. Performance

Data Shown: *Distribution of OoM Reduction based on geometric means of parent compound.*

Explanation: *The grey boxes and numbers show the 75th percentile and 25th percentile range (the middle 50%) of OoM results for each category. The black box shows the median value. The "whiskers" show the maximum and minimum value.*

Key Points

- Monitoring duration is defined as the time from the *initial injection event, or startup* of a thermal project, to the *final post-treatment monitoring event*. Monitoring durations for the 235 projects ranged from about 1 month (essentially 1 monitoring event following a single injection event) to more than 18 years for 1 bioremediation project. Only 18 sites had a monitoring duration of less than 3 months, while only 13 sites had a monitoring duration exceeding 10 years. The middle 50% range of monitoring durations was 1.2 to 5.7 years, with a median of 3.3 years.
- Performance was very consistent across the monitoring durations reported for the 235 projects. Concentration trends during the post-treatment monitoring period are described further in the evaluation of sustained treatment (Section 4.12).

4.9.3 Does the Number of Monitoring Points Matter?

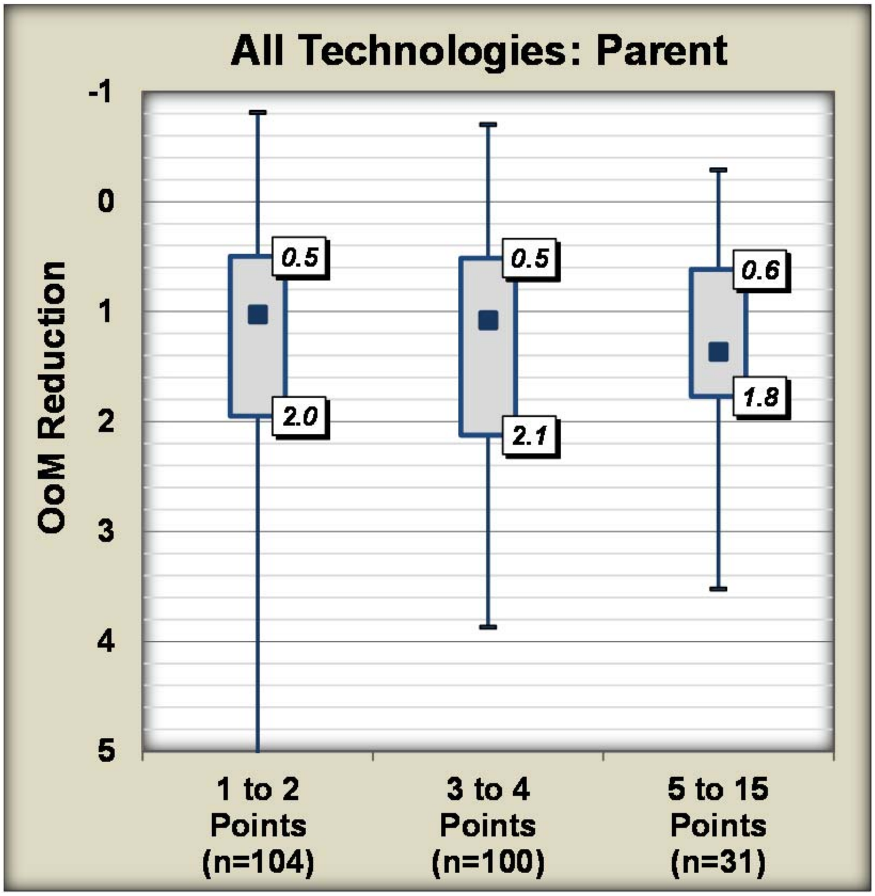


Figure 4.17. Number of Monitoring Points vs. Performance

Data Shown: *Distribution of OoM Reduction based on geometric means of parent compound.*

Explanation: *The grey boxes and numbers show the 75th percentile and 25th percentile range (the middle 50%) of OoM results for each category. The black box shows the median value. The "whiskers" show the maximum and minimum value.*

Key Points

- A greater number of monitoring points for a remediation project could be indicative of more thorough characterization of the treatment zone, and therefore better performance. The number of monitoring points for the 235 projects ranged from 1 to 15. 53 sites had only 1 monitoring point, while only 6 sites had 10 or more monitoring points.
- While the middle 50% range was fairly consistent at about 0.5 to 2 OoMs reduction, projects with 5 to 15 monitoring points within the treatment zone had a slightly better median performance at 1.4 OoM reduction vs. sites with fewer monitoring points, which had 1.0 to 1.1 OoM reduction. However, this difference was not statistically significant ($p=0.44$ based on t-test).

4.10 How Frequently Did In-Situ Remediation Projects Achieve MCLs?

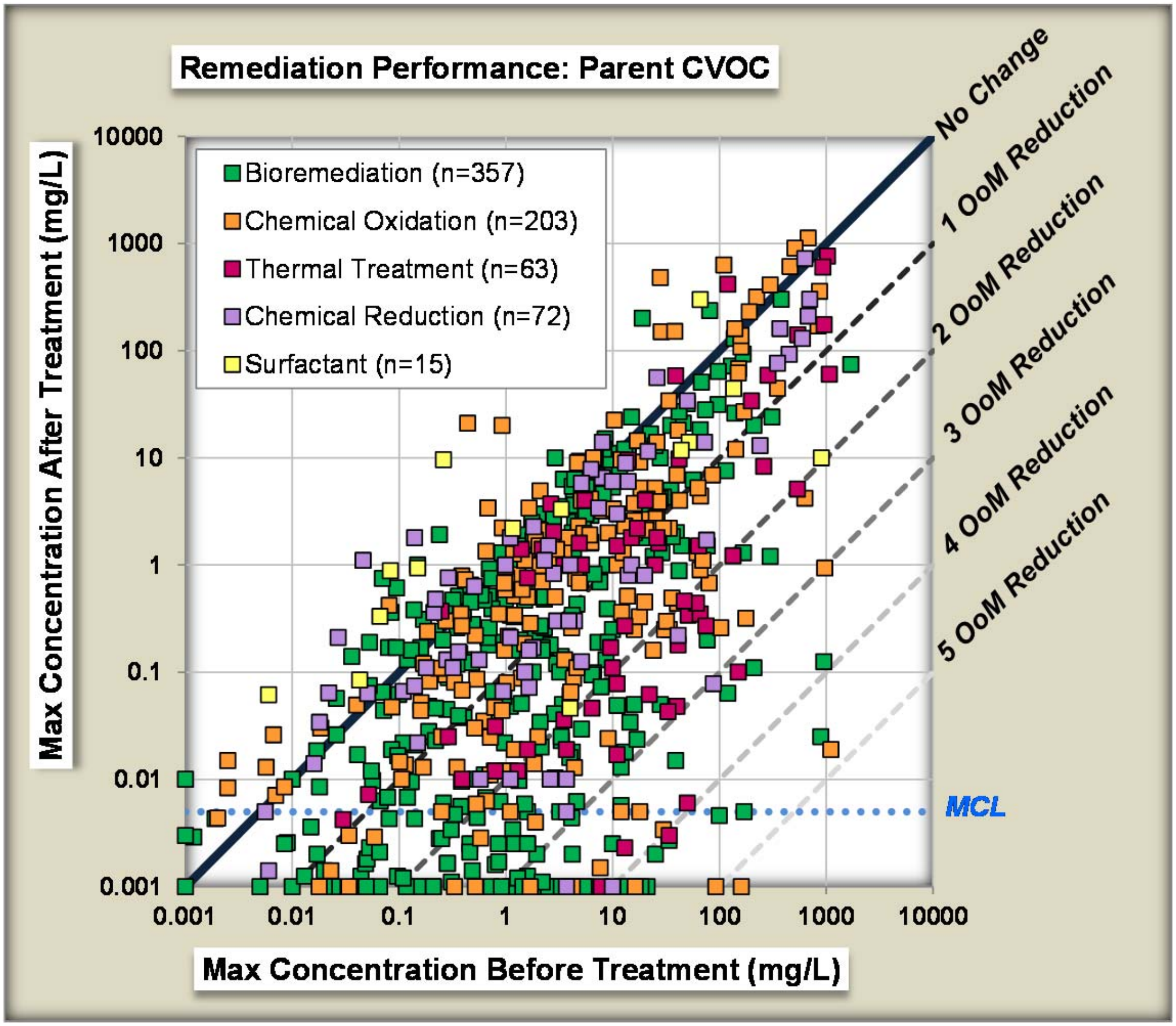


Figure 4.18. Change in Maximum Parent Compound Concentration for All 710 Wells Analyzed for this Project.

Data Shown: *Change in maximum concentration of parent compound.*

Explanation: *Each dot represents an individual well, showing the maximum before treatment concentration (X-axis) and after-treatment concentration (Y-axis). The dashed blue line shows the most common Maximum Concentration Limits (MCL) for chlorinated parent compounds, 0.005 mg/L.*

Key Points

- For site restoration, an important metric is for all the monitoring wells to achieve concentrations below Maximum Concentration Limits (MCLs). The prevalence in achieving MCLs in monitoring wells and sites was evaluated using the database.

Table 4.7a. Wells and Sites That Reached MCLs for Parent CVOC

	Total Number Of Monitoring Wells/Sites	Number of Wells/Sites That Reached MCLs for Parent CVOC based on Max. Concentration After Treatment	Number of Wells/Sites That Reached MCLs for Parent CVOC based on Max. Concentration After Treatment
Wells	710	146	21%
Sites	235	17	7%

Table 4.7b. Wells and Sites That Reached MCLs for Total CVOCs

	Total Number Of Monitoring Wells/Sites with Total CVOCs	Number of Wells/Sites That Reached MCLs for Total CVOCs based on Max. Concentrations After Treatment	Number of Wells/Sites That Reached MCLs for Total CVOCs based on Max. Concentrations After Treatment
Wells	434 *	27 *	6%
Sites	165 *	3 *	2%

* *Excludes wells/sites where only the parent CVOC was reported.*

Key Points (continued)

- Only 21% of 710 monitoring wells at 235 sites achieved a typical MCL of 0.005 mg/L for the parent CVOC based on maximum concentrations after treatment (Table 4.7a).
- Only 7% of 235 sites achieved MCLs at every monitoring well for the parent CVOC based on maximum concentrations after treatment (Table 4.7a). Of these 17 sites, 8 of them achieved a post-treatment maximum concentration of 0.001 mg/L (essentially non-detect).
- The 17 sites that did achieve MCLs at “all” wells for the parent CVOC were relatively special cases in that 10 of the 17 sites had only 1 monitoring well.
- Interestingly, 15 of the 17 sites had PCE as the parent compound, which may be more of a function that many of the smaller dry cleaner sites only were represented by one well that was sampled before and after treatment.
- The 17 sites that reached MCLs for the parent CVOC at all wells were treated using these technologies:
  - 13 Bioremediation sites,
  - 3 Chemical Oxidation sites, and
  - 1 Thermal Treatment site.

- An analysis of performance based on Total CVOCs was also performed (Table 4.7b). However, this analysis was problematic due to inconsistent availability of daughter product concentrations among the data sources (and even within individual sites) and the high variability in detection limits and concentrations of the daughter products. For example, sites often had elevated detection limits for daughter products with sporadic detections at concentrations sometimes higher and sometimes lower than the detection limits reported in other samples collected from the same monitoring well. Therefore, only detected concentrations of daughter products were quantified in the database, which further reduced the data population available for evaluation of Total CVOCs. Another option would have been to quantify non-detects as the detection limit, or one-half the detection limit, but doing so would have likely resulted in an over-estimate of actual concentrations due to the often elevated detection limits. As such, the analysis of Total CVOC performance data and associated outcomes carry greater uncertainty than the results based on parent CVOC concentrations.
- Only 6% of the 434 monitoring wells at 165 sites where Total CVOC data were available achieved a concentration of 0.005 mg/L for Total CVOCs based on maximum concentrations after treatment (Table 4.7b).
- Only 2% of 165 sites achieved MCLs at every monitoring well for the parent CVOC based on maximum concentrations after treatment (Table 4.7a).

4.11 What is the Cost of In-Situ Treatment?

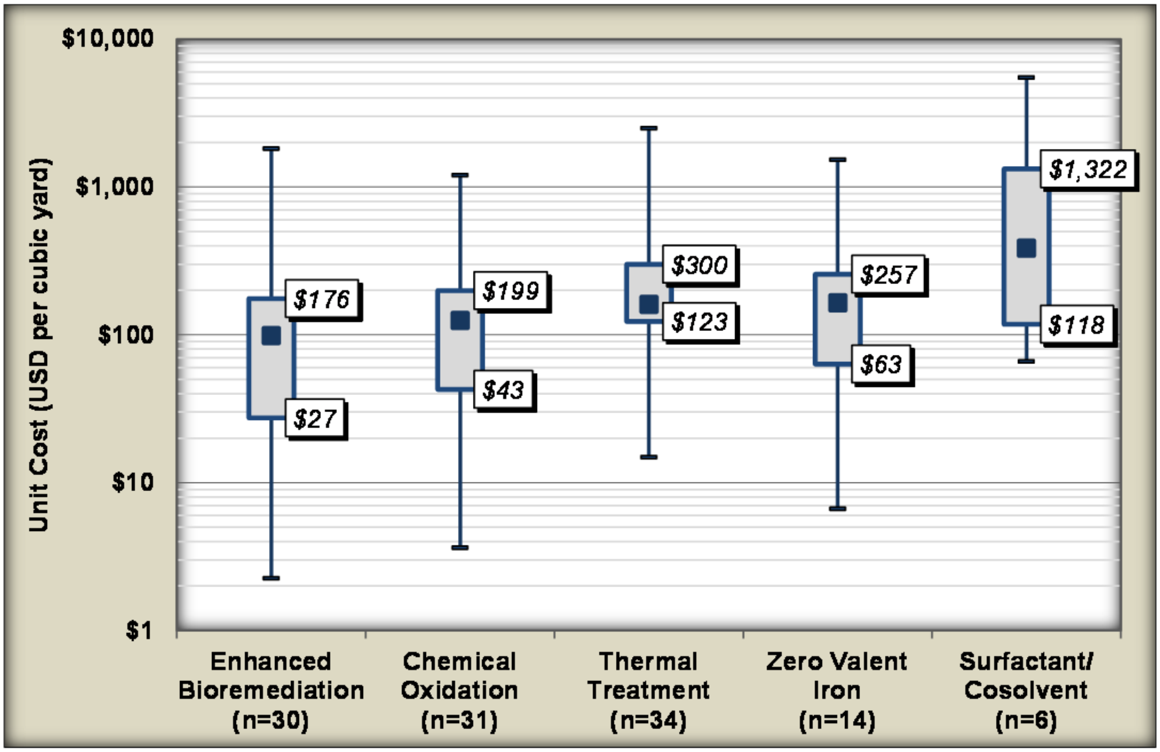


Figure 4.19. Unit Cost Distribution for 115 In-Situ Remediation Projects (Log Scale).

Data Shown: *Unit cost of in-situ treatment in US dollars per cubic yard.*

Explanation: *The grey boxes and numbers show the 75th percentile and 25th percentile range (the middle 50%) of OoM results for each category. The black box shows the median value. The "whiskers" show the maximum and minimum value.*

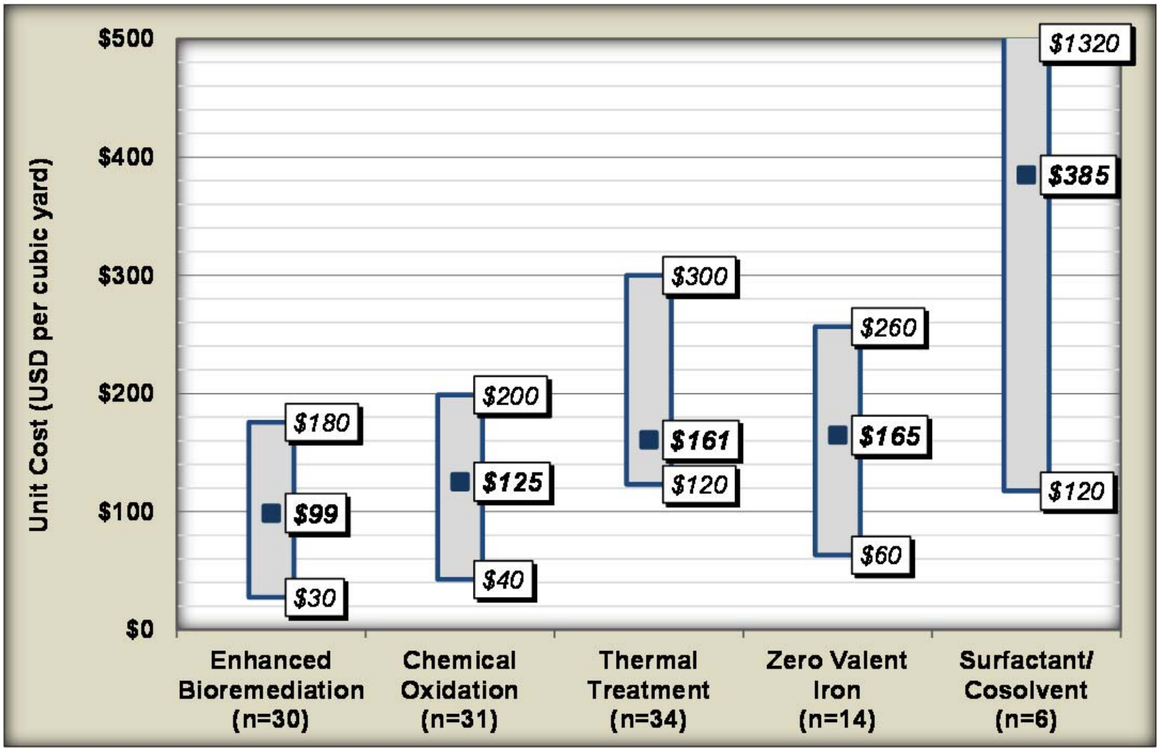


Figure 4.20. Middle 50% Unit Costs for 115 In-Situ Remediation Projects (Normal Scale).

Data Shown: *Unit cost of in-situ treatment in US dollars per cubic yard.*

Explanation: *The grey boxes and numbers show the 75th percentile and 25th percentile range (the middle 50%) of OoM results for each category. The black box and bold number shows the median value.*

Key Points

- Developing comparable unit costs for remediation projects is challenging as not all projects account for the same items. The costs reported in this section are the project team's best attempt to provide comparable, relative costs. In most cases the costs include design, permitting, construction, and operating. Typical groundwater monitoring and site characterization costs are not included.
- The unit costs for a typical in-situ remediation project ranges between $100 and $300 per cubic yard, but with some projects below $10 and some over $1000 per cubic yard (Figure 4.19).
- The median thermal project (n=34) was about 50% more expensive than enhanced bioremediation and chemical oxidation projects (Figure 4.20). The limited number of surfactant projects were much more expensive than other technologies.
- The performance of a remediation project did not seem to be correlated to unit costs (Figure 4.21). This is surprising, as more resources suggest more intense treatment that should translate to higher performance. But the remediation projects in this database may reflect costs that deal with external factors, such as access, high concentrations, difficult

hydrogeologic conditions, and therefore unit cost for treatment may not correlate to outcome at many sites.

- Remediation costs for bioremediation, chemical oxidation, and thermal treatment had about 40% to 50% positive correlation with treatment volume (Figure 4.22).
- Thermal projects had the highest total costs compared to bioremediation, chemical oxidation, and chemical reduction, with most of the thermal projects exceeding $1 million (Figure 4.22). Only a few bioremediation and chemical oxidation projects exceeded $1 million in total costs.

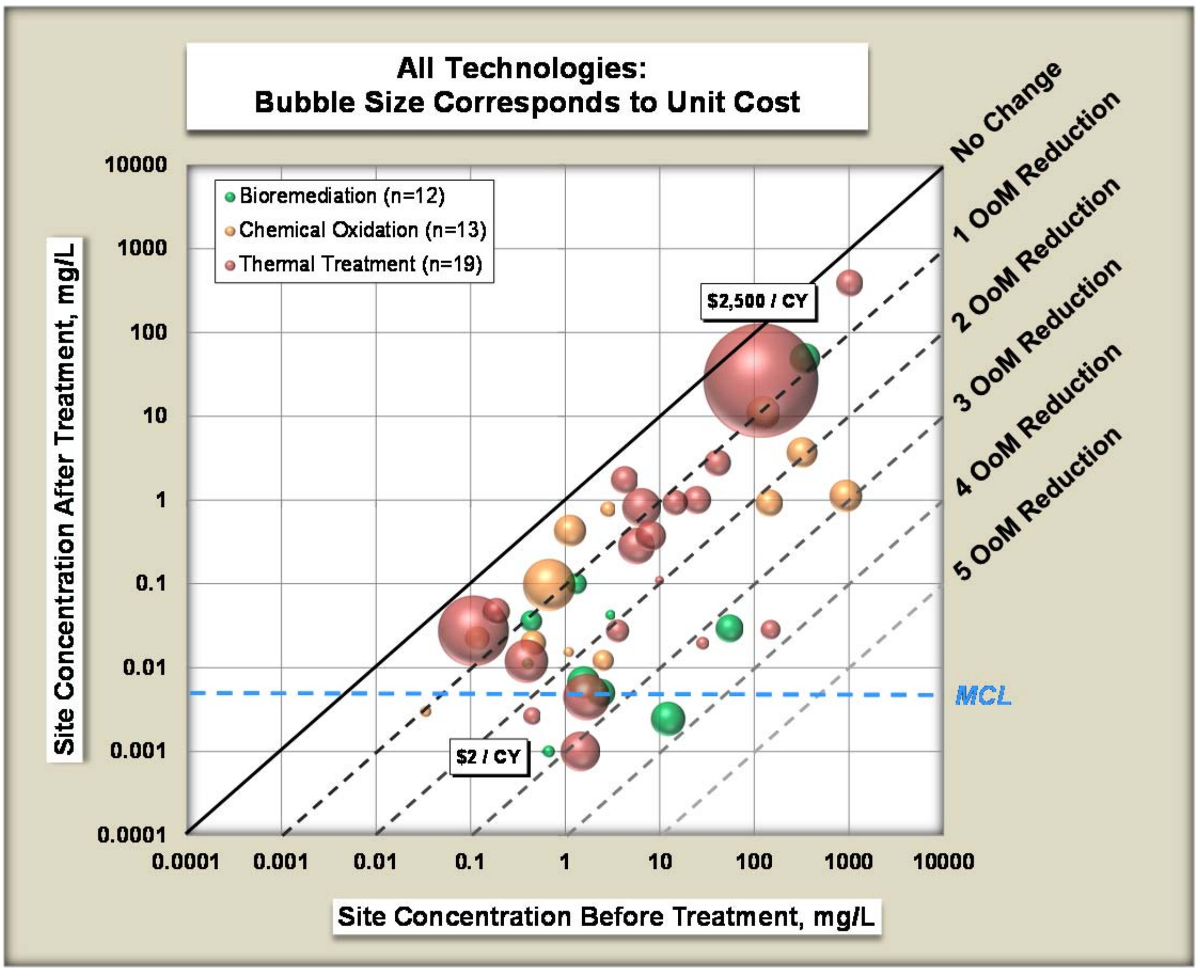


Figure 4.21. Remediation Performance vs. Unit Cost for Remediation Projects

Data Shown: *Change in geomean concentration of parent compound and unit cost for treatment (size of bubble).*

Explanation: *Each dot represents an individual remediation project, showing the geomean before treatment concentration (X-axis) and after-treatment concentration at the end of the sampling record (Y-axis). The size of the bubble correlates to the unit cost ($ per cubic yard) of the remediation project.*

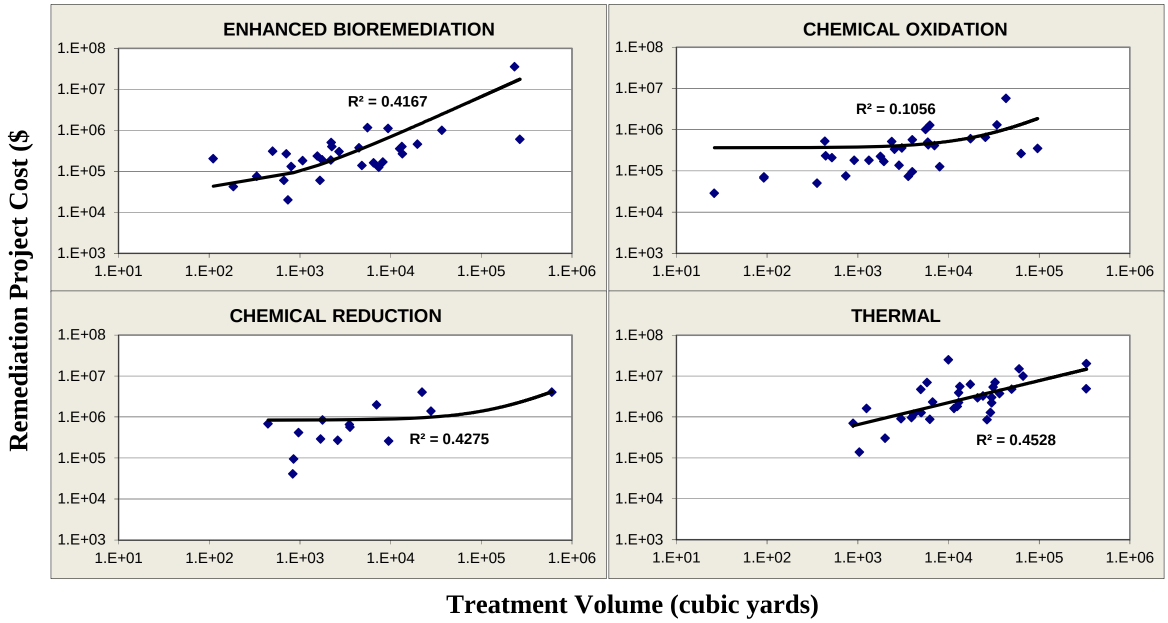


Figure 4.22. Total Cost of In-Situ Remediation Projects by Treatment Volume for Four Technologies

Data Shown: *Total cost of remediation cost vs. treatment volume*

Explanation: *Each dot represents the size and cost of an individual remediation project.*

4.12 Are the Benefits of In-Situ Remediation Sustained for Years, or Do Concentrations Eventually Rebound?

4.12.1 What is the Prevalence of Rebound for Different Technologies?

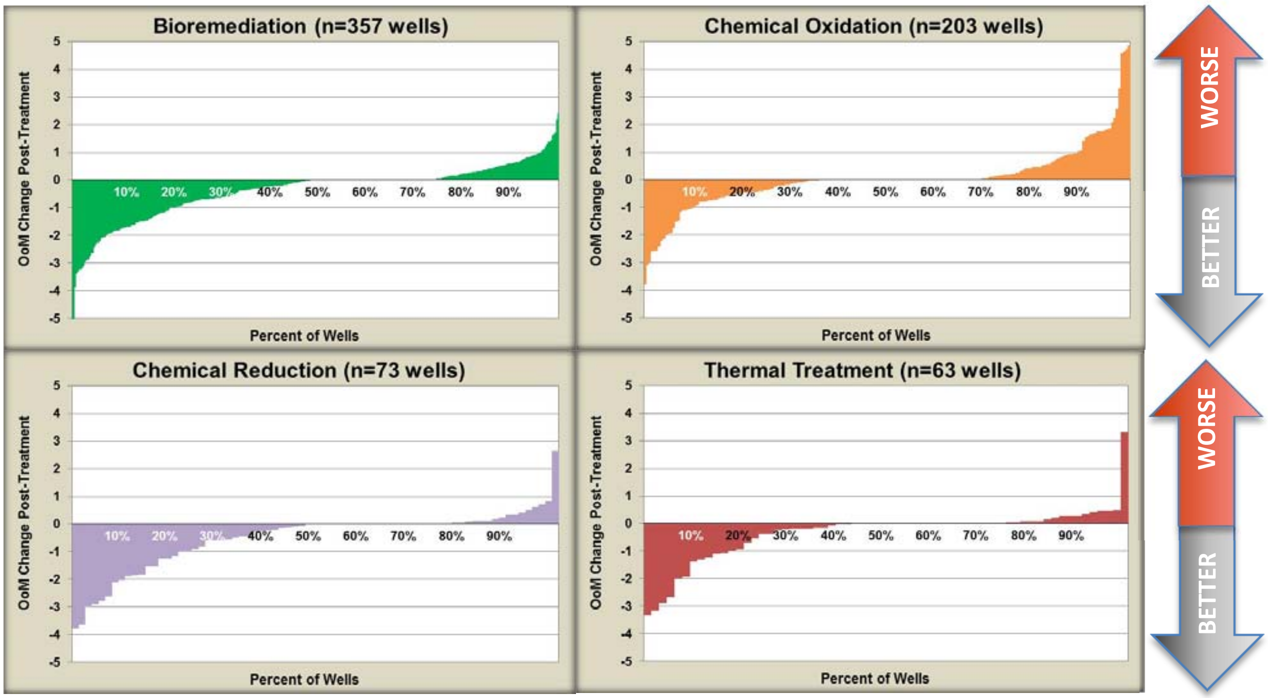


Figure 4.23. Rebound Frequency by Monitoring Well for Four In-Situ Remediation Technologies

Data Shown: *Frequency of rebound in monitoring wells, showing change in geomean parent concentrations from first monitoring period after actual remediation activities are terminated to last monitoring period (from 1 to 12 years).*

Explanation: *More colored bars above the "0" line in each panel shows rebound.*

Key Points

- Rebound can be defined in many ways. For this project it was defined as an increase in concentration (expressed as a change in OoMs) from first monitoring period after actual remediation activities are terminated to last monitoring period**.** This ranged from as little as one year for some sites to up to around 12 years at a few sites.
- With this definition, rebound was observed in a few monitoring wells for all technologies.
- Chemical oxidation projects appeared to have the most rebound, with about 30% of the monitoring wells showing rebound. About 10% of the chemical oxidation monitoring wells had rebound of 2 orders of magnitude compared to the post-treatment concentrations.
- Bioremediation had the next highest rebound, with about 25% of wells showing rebound. The severity of rebound was not as high as chemical oxidation, however.
- Thermal and chemical reduction project appeared to have the least rebound.

- The performance at bioremediation sites with shorter post-treatment monitoring records (<3 years) was similar to that observed at sites with longer post-treatment monitoring records (3 to 12 years) (see Figure 4.24). The median OoM reduction for sites with less than 3 years of post-treatment monitoring data (median = 1.1) is not significantly different than the median OoM reduction for sites with longer monitoring periods (median = 1.0) (p=0.80 based on Mann Whitney test).
- There were a significant number of sites where the post-treatment concentration fell below the MCL for PCE/TCE, including 26 (31%) of the sites with shorter monitoring periods and 13 (38%) of the sites with longer monitoring period. There were only 4 sites (5%) with less than 3 years of monitoring data where the post-treatment concentration was greater than the pre-treatment concentration.
- This evaluation also shows that there is little reason to expect additional rebound if longer-term monitoring (i.e., more than 3 years) is implemented. This pattern should help alleviate stakeholder or regulatory concerns that a shorter-duration monitoring program (i.e., less than 3 years) would “miss” rebound, and it suggests that remediation performance can be adequately assessed within 3 years.

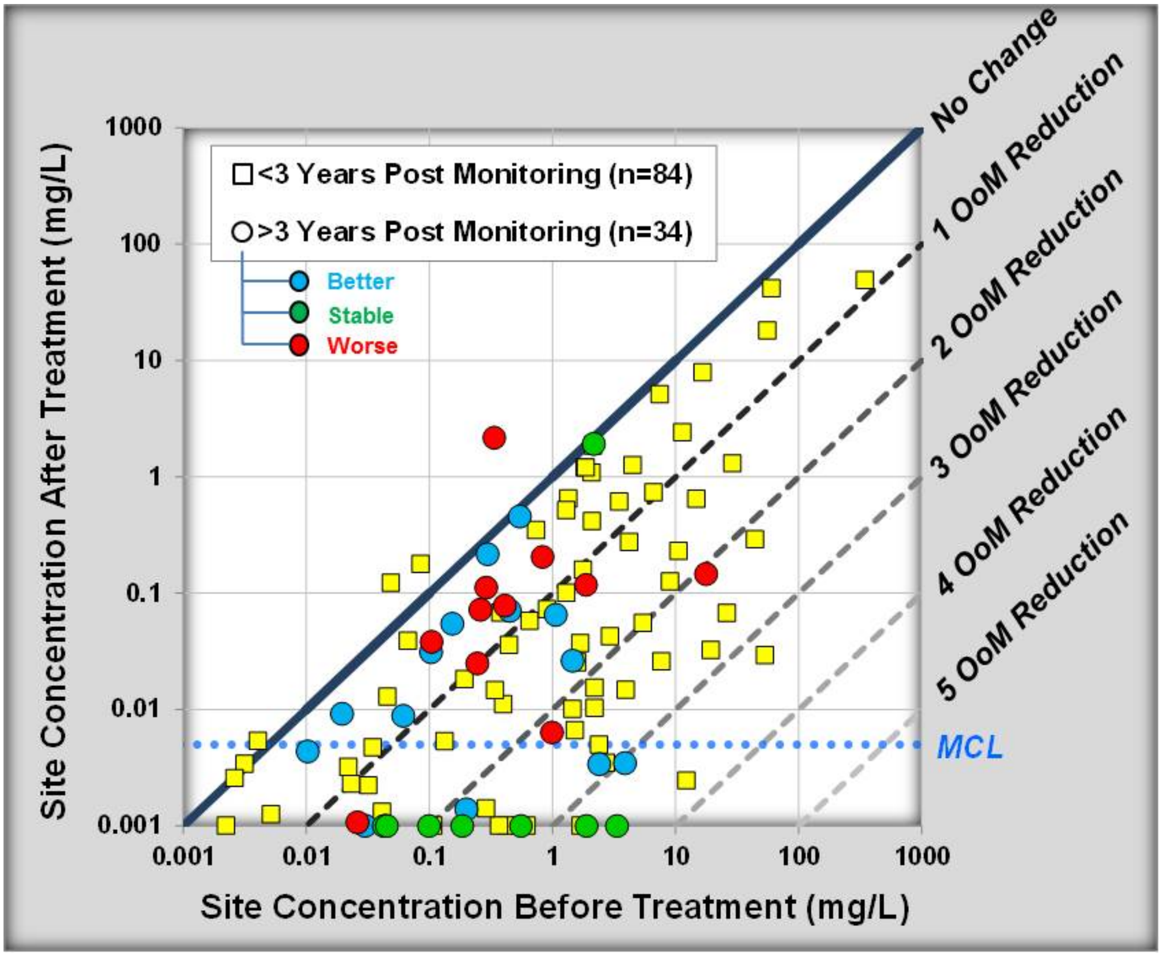


Figure 4.24. Before-Treatment and After-Treatment Concentrations at Bioremediation Sites with Short Post-Treatment Monitoring Records vs. Long Post-Treatment Monitoring Records.

Data Shown: *Change in maximum concentration of parent compound at enhanced bioremediation sites.*

Explanation: *Each dot represents an individual site, showing the maximum before-treatment concentration (X-axis) and after-treatment concentration at the end of the sampling record (Y-axis). Square symbols represent sites with less than 3 years of after-treatment monitoring; round symbols show sites that enjoyed continued reductions in concentration (blue circles); green showed relatively stable concentrations (green circles); and red show sites where concentrations increased over a 3+ year after-remediation monitoring period.*

4.12.2 What is Bioremediation Sustained Treatment and How Often is It Observed?

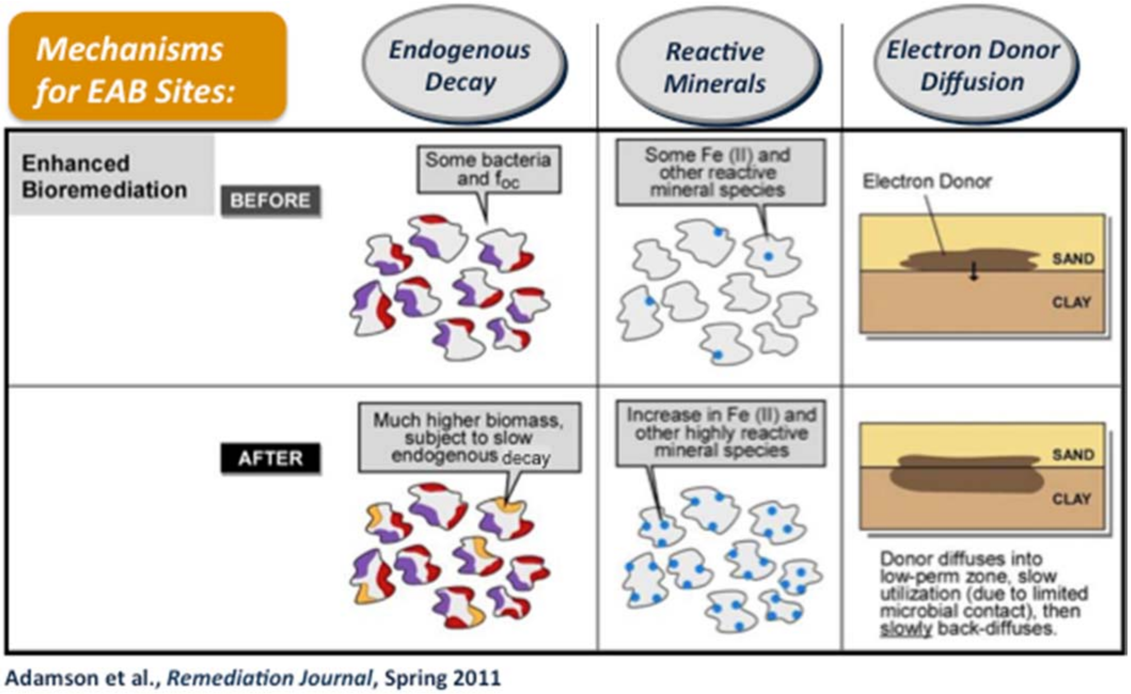


Figure 4.25. Sustained Treatment Mechanisms at Bioremediation Sites

$$OoM\ Reduction = -\log\left(\frac{C_{Post}}{C_{Pre}}\right)$$

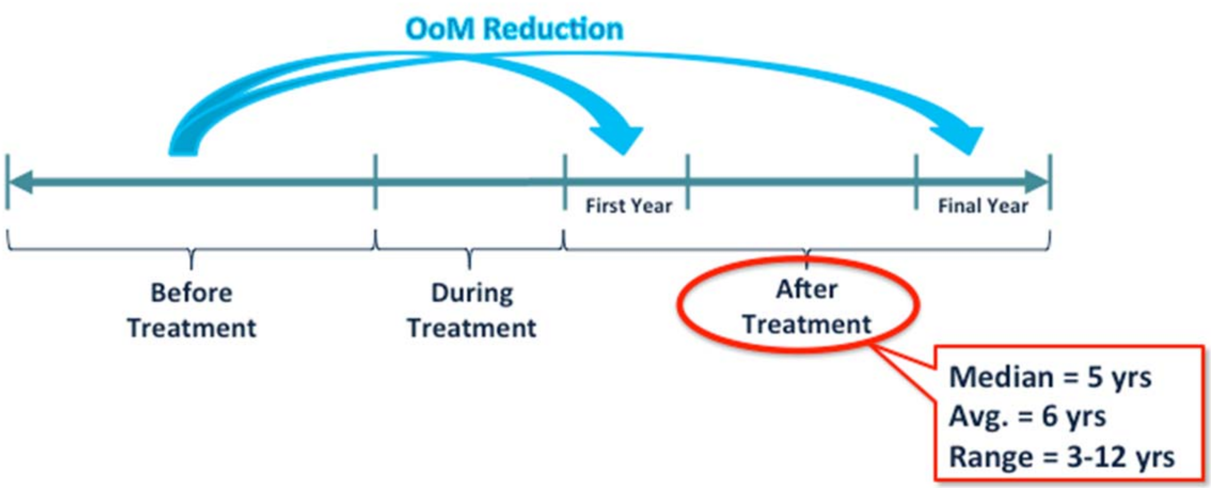


Figure 4.26. Basis for Sustained Treatment Analysis Shown in Figure 4.27

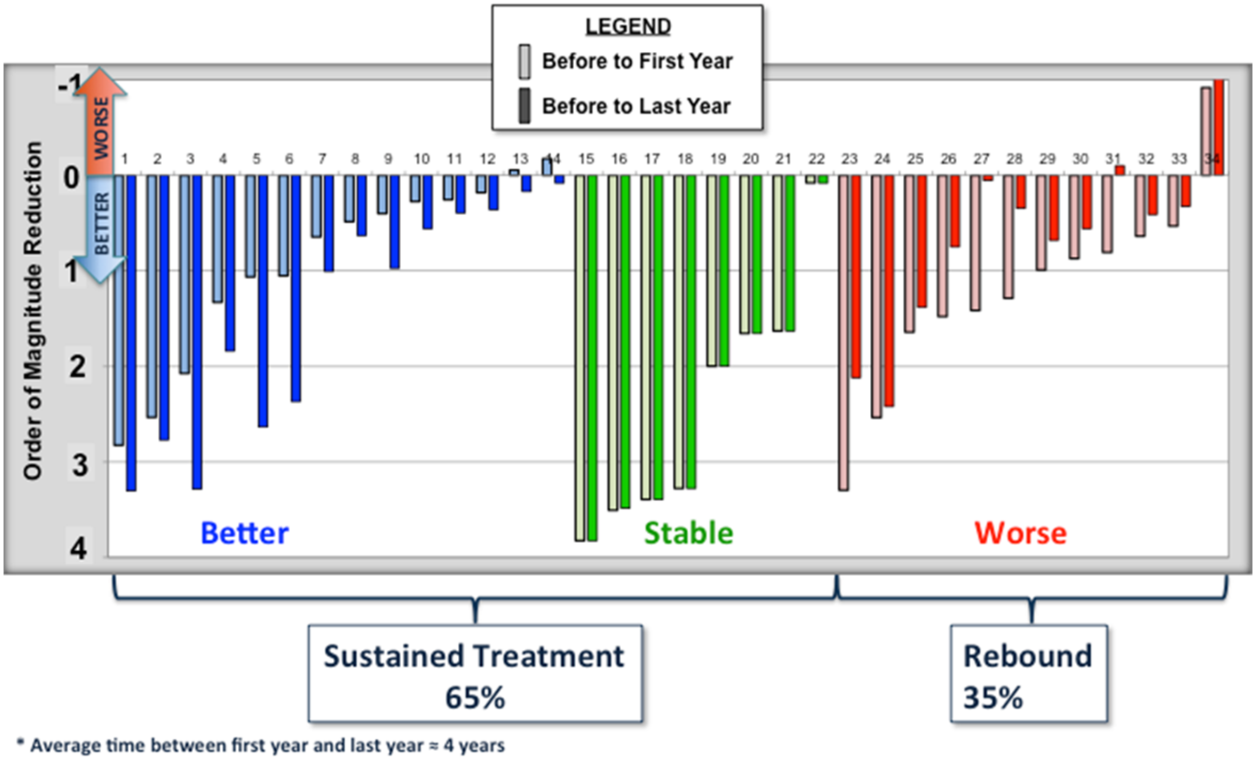


Figure 4.27. Analysis of Sustained Treatment at 34 Bioremediation Sites with Long-Term After-Treatment Data

Data Shown: *Order of Magnitude (OoM) reduction in geomeans of parent compound.*

Explanation: *Two bars are shown for each site with enough after-treatment data to be analyzed for sustained treatment. The Left Bar (light colored) shows observed OoM reductions from before-treatment parent concentrations to first year after treatment ends; the Right Bar shows before-treatment parent concentrations to last year of monitoring (typically 6 years after treatment ends).*

Key Points

- Sustained treatment is the continuation of attenuation processes at sites after active treatment ends due to the effects of: 1) endogenous decay; 2) activation of reactive minerals; and 3) electron donor diffusion (Figure 4.25). Since most of these support and/or result from microbial activity, sustained treatment is of particular interest at bioremediation sites.
- A total of 34 bioremediation sites had enough post-remediation concentration data (at least 3 years, median of 5 years, maximum of 12 years, see Figure 4.26) to analyze sustained treatment.
- A total of 14 of these sites improved over the long after remediation-period, and 8 were about the same. A total of 12 of these bioremediation sites had increasing concentrations (rebound) during the after-remediation period. This suggests that 65% of the sites may

have exhibited sustained treatment, while the remaining 35% of the bioremediation sites exhibited rebound.

- For the entire set of sites where rebound was observed, the median concentration reduction over the post-treatment monitoring period changed from 90% (after the first year) to 67% (after the last year). This suggests that the degree of concentration rebound is generally modest at sites where it occurs.
- Overall, performance at bioremediation sites did not significantly change (p=0.69 based on two-sided Wilcoxon Signed Rank test) when the before-to-first-year-after-treatment is compared to before-to-last-year-of-monitoring (median of four years of monitoring) (Figure 4.28).
- The results suggest that sustained treatment processes are providing some benefit by preventing concentration rebound at the majority of these sites, but that these processes do not necessarily contribute to further concentration reductions except at a subset of sites.

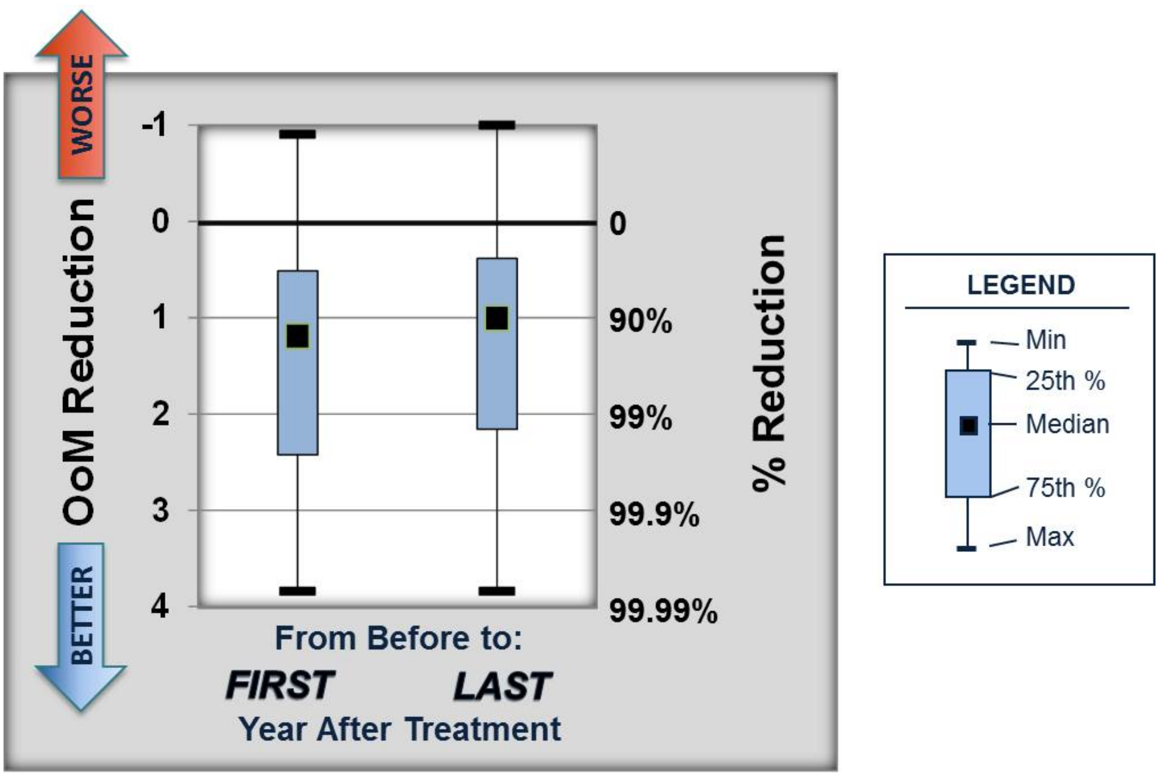


Figure 4.28. Analysis of Sustained Treatment at 34 Bioremediation Sites with Long-Term After-Treatment Data

Data Shown: *Order of Magnitude (OoM) reduction in geomeans of parent compound.*

Explanation: *The grey boxes and numbers show the 75th percentile and 25th percentile range (the middle 50%) of OoM results for each category. The black box shows the median value. The "whiskers" show the maximum and minimum value.*

4.13 How Does Active Remediation Compare to Monitored Natural Attenuation (MNA)?

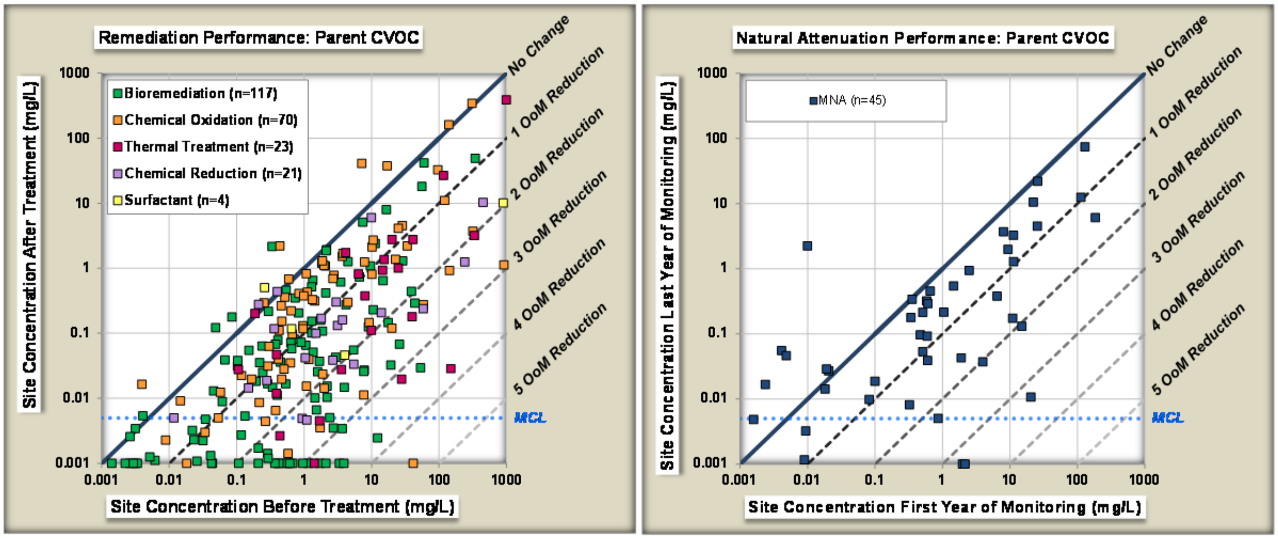


Figure 4.29. Performance of 235 Active Remediation Projects vs. 45 Monitored Natural Attenuation Projects

Data Shown: *Parent compound geomean concentration before and after treatment for remediation sites (left panel) and geomean of first year and last year concentrations for MNA sites (right panel).*

Explanation: *Each dot represents an individual project, showing the geomean before treatment concentration (X-axis) and after-treatment concentration at the end of the sampling record (Y-axis). The left panel is the same one shown in Figure 4.1. The right panel shows the results from 45 MNA sites.*

Key Points

- The performance of MNA projects can be compared to active remediation projects using similar analysis and metrics as was used for evaluating performance at active remediation projects. The change in the geometric mean of the parent compound concentration for the first year to the last year of the MNA monitoring record was about 0.7 OoMs (Figure 4.28 and Table 4.8). This is only slightly lower than the median OoM reduction of 1.1 observed for all 235 of the remediation projects (see Table 4.1).
- MNA Sites had lower before treatment concentrations (median of 0.67 mg/L) compared to the active remediation sites (median of 1.3 mg/L), indicating that MNA is generally applied at lower concentration sites.
- A key differentiator is the time required to achieve the observed OoM reductions. For the active projects, the median treatment duration was 0.5 years. For the MNA projects, the median monitoring duration (analogous to "treatment" duration) was 8.7 years and ranged from 4.1 to 15 years.

- Using a very crude extrapolation of the medians, about 14 years would be required for the median OoM reduction at MNA sites to reach a value of 1.1 OoM reduction, the median performance achieved by active remediation. Therefore, active remediation speeds up the remediation process by about 13.5 years assuming no rebound or sustained treatment for the active projects, continued treatment by MNA, and holds only for this particular metric (geometric means of the parent compound).
- This type of analysis comparing the "time gained" toward achieving groundwater restoration by active remediation was discussed in Newell et al., 2006.

Table 4.8. Change in Parent Compound Geometric Mean Concentrations for Four Active In-Situ Remediation Technologies vs. MNA.

	Parent Median Geomean Concentration Before Treatment (mg/L)	Parent Median Concentration After Treatment (mg/L)	Median % Reduction in Geomean of Parent Compound in Treatment Zone	Median OoM Reduction Geomean of Parent Compound in Treatment Zone
Enhanced Bioremediation	0.74	0.027	96%	1.4
Chemical Oxidation	1.1	0.27	77%	0.6
Thermal Treatment	10	0.20	98%	1.7
Chemical Reduction	1.8	0.13	93%	1.1
MNA*	0.67	0.13	81%	0.7

* *Geomean concentrations for MNA sites based on First Year and Last Year of monitoring record.*
Median treatment time for 45 MNA Projects: 8.7 years.
Median treatment time for 235 Active Remediation Projects: 0.5 years.

4.14 Have We as an Industry Gotten Better at Remediation Over Time?

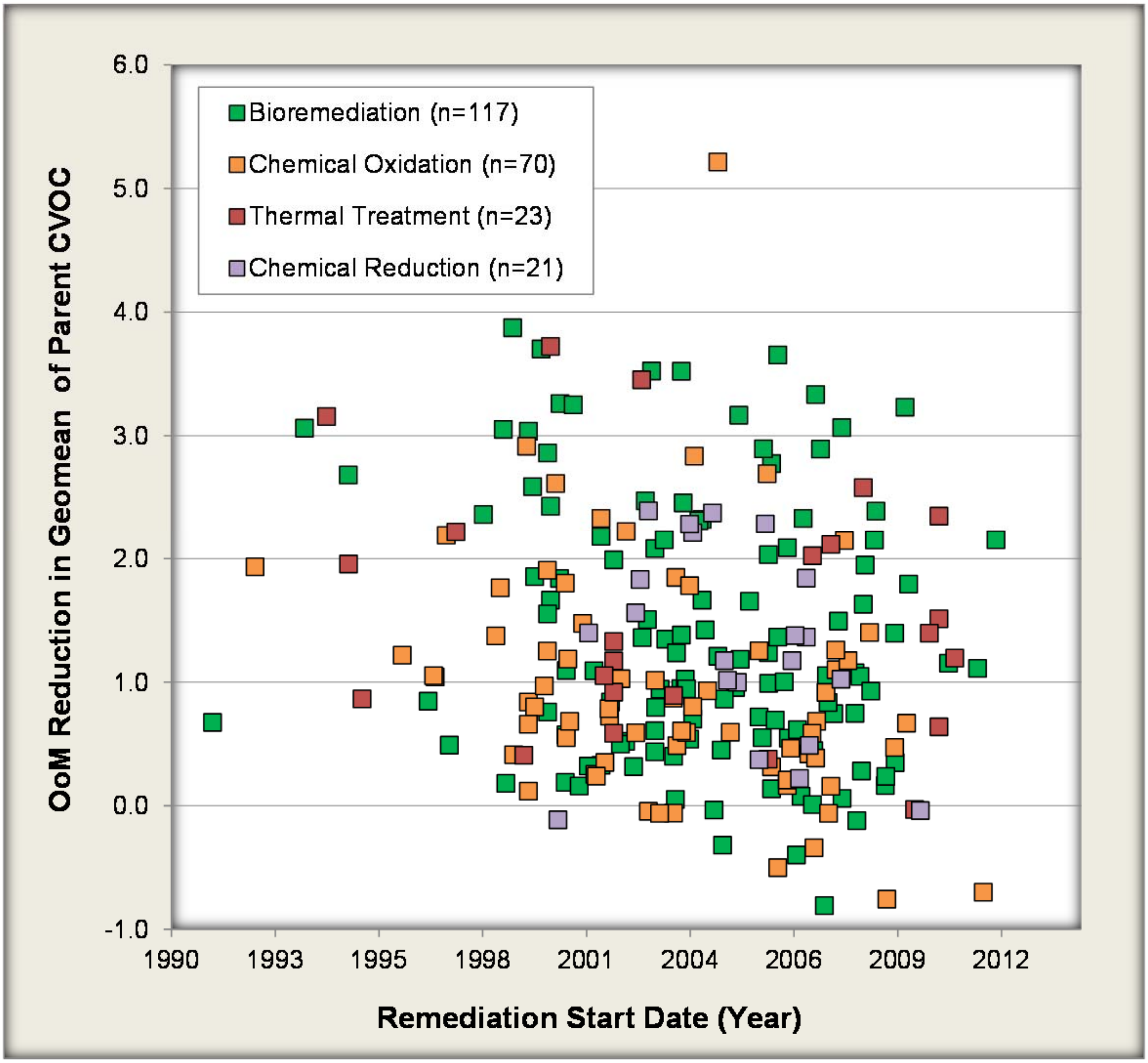


Figure 4.30. Performance of 235 Active Remediation Projects vs. Time Treatment Began

Data Shown: *OoM reduction in geomean concentration of parent compound by year that treatment began.*

Explanation: *Each dot represents an individual remediation project, showing the change in before and after remediation concentrations as OoM reduction. The X-axis is the time the remediation project began and Y-axis is the OoM reduction achieved by the remediation project.*

Key Points

- One question that was asked of the project team was "has the remediation profession gotten better over time?" In other words, has our increased knowledge of subsurface hydrogeology,

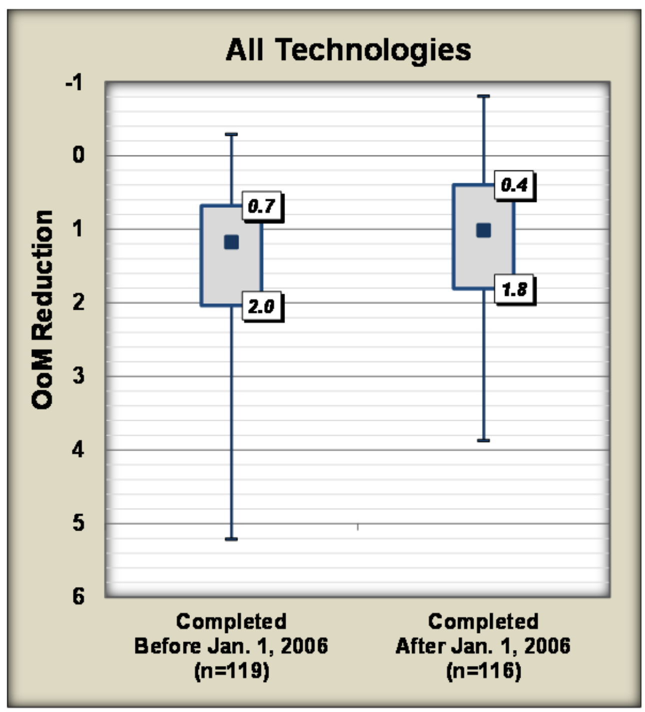
transport, chemistry, biology, and other factors increased the performance of our remediation projects over time? Have new concepts such as high resolution characterization, matrix diffusion, and the life cycle of chlorinated solvent sites made us better as industry?

- The 235 active remediation projects in this data suggest that there is not a strong trend in how well remediation projects appear to perform over time. A statistical evaluation of the data in Figure 4.30 using the non-parametric Spearman test shows that there is a statistically-significant negative correlation between performance and later start dates ($p=0.013$) but that the relationship is weak ($rho=-0.16$)
- Looking at this question in a slightly different way, Figure 4.31 shows the distribution of remediation projects in terms of OoM performance for projects that were *completed* before 2006 vs. those completed after 2006. There is little apparent difference in the performance of the projects in the "Old Project" category vs. "Recent Project" category. However, using the Mann-Whitney test, the median OoM reduction for the "Old Project" dataset (1.2) was determined to be higher than the value for the "Recent Project dataset (1.0) ($p=0.03$).
- This suggests that the fundamental constraints that preclude achieving restoration of sites (reaching MCLs) are still present in remediation projects being conducted today.

Figure 4.31. Performance of 217 Active Remediation Projects: Old Projects vs. Recent Projects

Data Shown: *OoM reduction distribution based on geomeans of parent compound.*

Explanation: *The grey boxes and numbers show the 75th percentile and 25th percentile range (the middle 50%) of OoM results for each category. The black box shows the median value. The "whiskers" show the maximum and minimum value. Old projects (left box) were completed between 1991 and 2005; new projects (right box) were completed in 2006 and beyond.*



4.15 What "Percent Complete to Restoration" Does a Typical Active In-Situ Remediation Project Achieve?

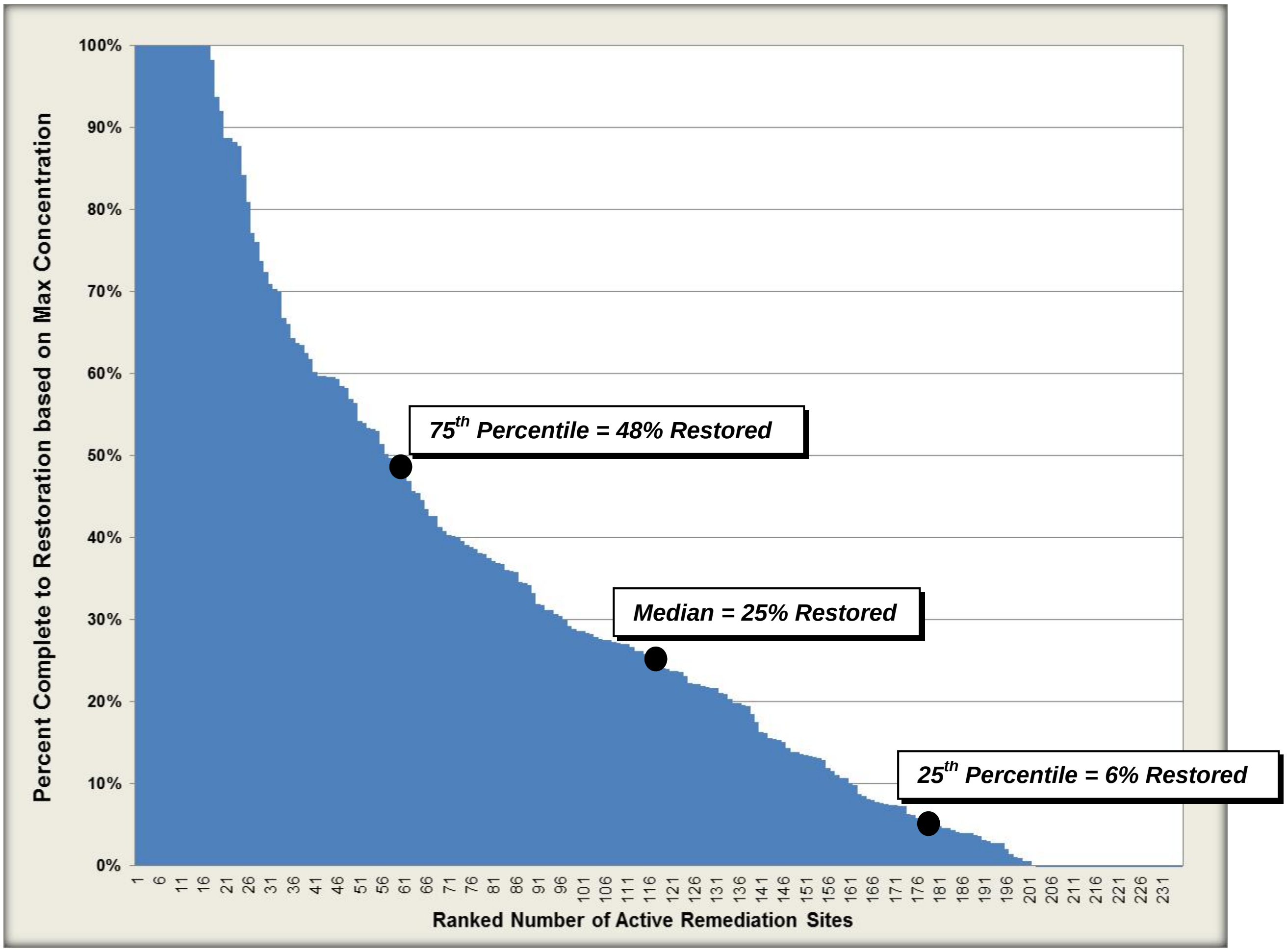


Figure 4.32. Approximate Percent Complete to Groundwater Restoration Achieved for 235 Active Remediation Sites Using Order of Magnitude Metric

Data Shown: *Percent complete to restoration based on maximum concentrations after treatment of parent compound in the treatment zone, where the percent to restoration is calculated relative to a 0.005 mg/L target concentration (values greater than 100% and less than 0% not shown)*

Explanation: *Each bar is an individual remediation project and assumes the OoM reduction in the maximum concentration of the parent compound can be used to calculate an approximate "Percent Complete to Restoration" metric. The sites that are at 100% achieved an after-remediation project maximum concentration less than the MCL; sites at 0% showed an increase in the after-remediation project maximum concentration compared to before treatment.*

Key Points

- The OoM metric assumes that remediation is a log-normal type activity, where progress can be measured by the number of OoMs a project achieves.
- If one extends the OoM metric all the way to a typical low part per billion cleanup standard (in this case we assume a 0.005 mg/L MCL), then two numbers can be compared: 1) the number of OoMs a remediation project actually achieved; and 2) the number of OoMs that are still required to reach a cleanup goal. Then the percent complete can be estimated using #1 divided by the sum of #1 and #2. For example, if the before treatment parent compound concentration was 5.000 mg/L; and if the project reduced concentrations to 0.05 mg/L, then 2 OoMs were achieved. However, to reach the metric used in this calculation (an MCL at 0.005 mg/L), an additional 1 OoM is required. Therefore this project achieved a 67% (1 ÷ 3) "percent complete to restoration."
- This calculation is sensitive to the choice of the metric (we used before and after treatment maximum concentrations as maximums are more relevant for a regulatory performance metric (see Section 4.7.1). The calculation is also sensitive to the cleanup target concentration (we used 0.005 mg/L, even though some sites are controlled by compounds that may have different MCLs).
- The "percent complete to restoration" metric is an indication of how far the site has to go achieve MCLs at the site. This number has been used in litigation cases to estimate what percentage of the required total remediation cost has been expended with the existing project, assuming that active remediation will be pursued until MCLs are reached. However, if more passive treatment approaches are used (e.g., MNA or containment) to manage the residual contamination, two implications are: 1) remediation timeframes will be longer; and 2) future costs are likely to be lower.
- The calculation does not account for any sustained treatment, source attenuation, or treatment train type projects after the original remediation project is complete.
- If one accepts these assumptions and limitations, it suggests that current practice as reflected in the 235-site database typically gets between 6% and 48% (this is the middle 50% of the sites shown in Figure 4.32), with a median of 25% of "Percent Complete to Restoration".

5.0 RESULTS OF SPECIAL TOPIC STUDIES

This section describes the results of special studies that were conducted to further assess in-situ remediation performance at CVOC groundwater sites.

5.1 Results of Focused Field Studies

5.1.1 Sampling and Testing Results

Focused field studies were performed at two sites: Tinker Air Force Base (AFB) in Oklahoma City, Oklahoma and Altus AFB in Altus, Oklahoma. The two sites are located approximately 120 miles apart and have similar hydrogeologic settings.

At Tinker AFB, two areas were selected for testing: Fire Training Area 2 (FTA-2) and the Driving Range Area (DRA). At FTA-2, a large-scale enhanced bioremediation pilot test using a slow-release carbon substrate (emulsified soybean oil) was conducted in 2003, with the last sampling event conducted in 2005. At the DRA, a large-scale, multiple technology pilot test was conducted in 2003-2004, with the last sampling event in 2006. The DRA project consisted of three side-by-side treatments including enhanced bioremediation using a soluble carbon substrate (lactate), chemical oxidation using Fenton's reagent, and chemical oxidation using potassium permanganate. At Altus AFB, the groundwater source area associated with Building 323 was selected for testing. At this site, a full-scale enhanced bioremediation project using a slow-release carbon substrate (emulsified vegetable oil) was implemented in 2008, with the last sampling event in 2011.

5.1.1.1 Tinker AFB Results for FTA-2

At Tinker AFB Fire Training Area 2, groundwater samples were collected from 1 monitoring well, SIW-01, located within the former bioremediation treatment zone (see Figure 5.1). Groundwater in this area was treated via injections of emulsified vegetable oil in November 2003. Post-treatment groundwater samples were collected 3 times over a 2 year period between November 2004 and September 2005. Our long-term post-treatment sampling event was conducted in June 2103, almost 10 years after treatment and nearly 8 years after the last sampling event. Samples were tested for a broad range of parameters to evaluate the potential for on-going bioremediation (i.e., sustained treatment) vs. rebound. Table 5.1 summarizes the historical and recent sampling results.

Figure 5.1. Tinker AFB, Fire Training Area 2 Location Map

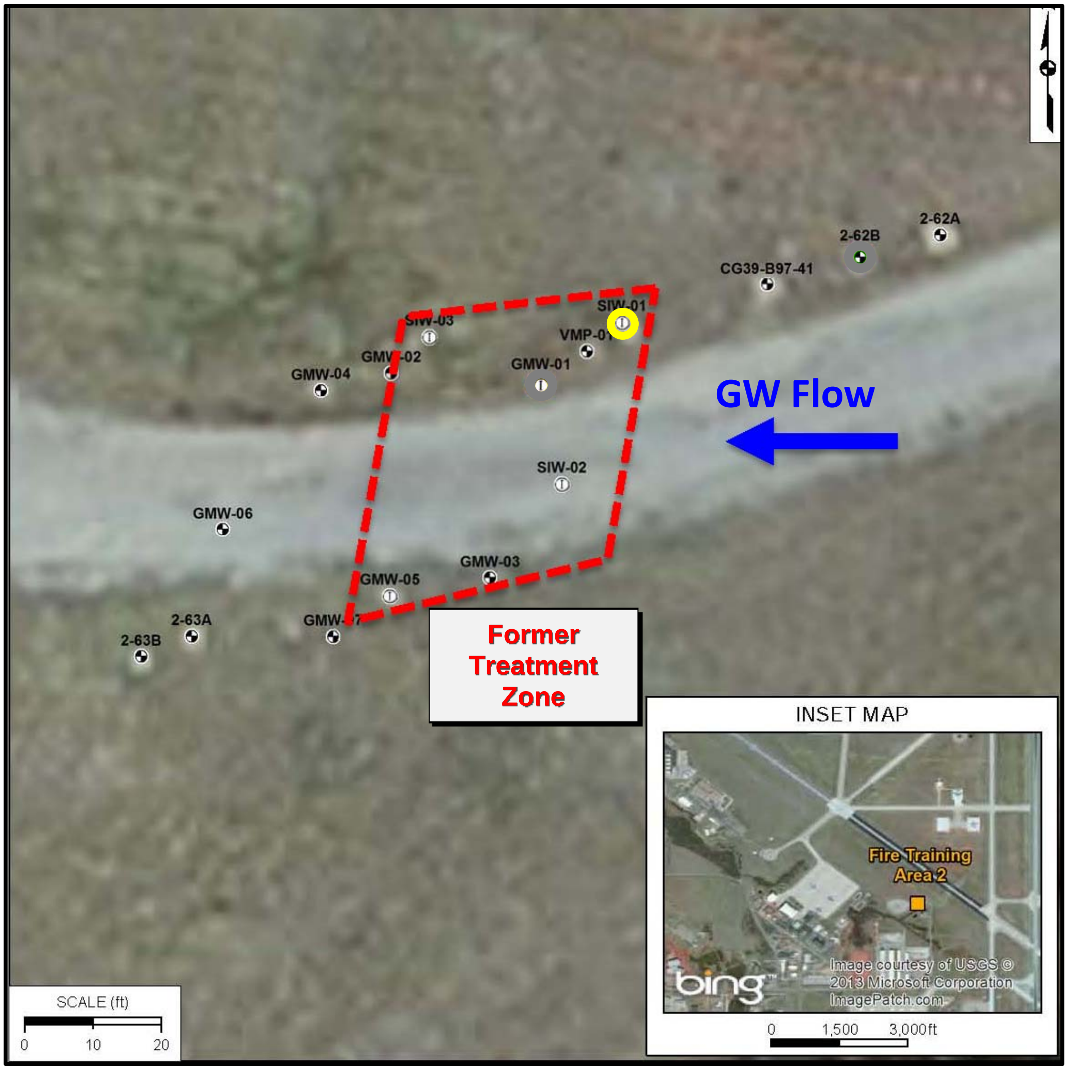


Table 5.1. Historic and Recent Groundwater Sampling Results at Tinker AFB, Fire Training Area 2, Well SIW-01

Site: Well ID	Tinker AFB, FTA-2: SIW-01				
Sample Date	**10/20/2003**	**5/11/2004**	**11/16/2004**	**9/21/2005**	**6/5/2013**
Time After EVO Injection (years)	**-0.1**	**0.6**	**1**	**2**	**10**
CVOCs	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Tetrachloroethene (PCE)	<0.28	<0.00083	<0.00083	<0.0012	<0.00037
Trichloroethene (TCE)	**7.8**	**0.052**	**0.056**	**0.073**	**0.0026**
cis-1,2-Dichloroethene (cis-DCE)	**0.74**	**0.0167 J**	**0.048**	**0.125**	**4.5**
trans-1,2-Dichloroethene (trans-DCE)	**0.036 J**	<0.00093	<0.00093	**0.004 J**	**0.029**
Vinyl chloride	<0.22	<0.00058	<0.00058	**0.0045 J**	**0.051**
Dissolved Gases	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Methane	**0.52**	**0.61**	**4.3**	**12**	**1.9**
Ethane	**0.0034**	**0.00049**	**0.001**	**0.000069**	<0.004
Ethene	**0.012**	**0.00078**	**0.00026**	**0.00031**	<0.0057
Acetylene	--	--	--	--	<0.056
Inorganics	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Chloride	**340**	**160**	**160**	<6	**150**
Nitrate	**5.4**	<0.05	<0.05	<0.1	<0.023
Sulfate	**190**	**14**	--	**4**	**1.3 J**
Alkalinity (as $CaCO_3$)	**318**	--	--	**396**	**890**
Manganese, Dissolved	**0.5**	**20**	**0.8**	**2.7**	**1.1**
Calcium, Dissolved	--	--	--	--	**92**
Iron (Total), Dissolved	--	--	--	--	**28**
Magnesium, Dissolved	--	--	--	--	**110**
Potassium, Dissolved	--	--	--	--	**13**
Sodium, Dissolved	--	--	--	--	**170**
Organic Carbon	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Total Organic Carbon	<5	**3600**	**3800**	**2900**	**93**
Dissolved Organic Carbon	--	--	--	--	**69**
Microbial					
Total Biomass (cells/mL)	**1.0 E+4**	**1.8 E+7**	**5.3 E+6**	--	**2.7 E+7**
DNA (ug/L)	**0.04**	**72**	**21**	--	**108**
Dehalococcoides (cells/L)	--	--	--	--	<1.0 E+4
Field Measurements					
pH (Standard Units)	**8.53**	**5.07**	**5.27**	**5.26**	**6.14**
Temperature (Degrees C)	**19.8**	**17.7**	**18.6**	**21.4**	**20.9**
Conductivity (mS/cm)	**2.1**	**4.4**	**4.0**	**3.6**	**2.0**
Dissolved Oxygen (mg/L)	**0.5**	**0.12**	**0.55**	**0.33**	**5.01**
Oxidation-Reduction Potential (mV)	**-181**	**-72**	**141**	**-108**	**-158**
Ferrous Iron (mg/L)	**0.58**	**140**	**28.3**	**209**	**2.25**

Results indicate that concentrations of TCE, the parent CVOC, had declined by about 2 OoMs after 2 years of post-treatment monitoring. Our sampling results, nearly 10 years post-treatment, indicated that TCE declined by an additional 1.4 OoMs, resulting in a total reduction of approximately 3.5 OoMs. These results suggest better than average performance was achieved initially by the remediation project, and after 10 years, the OoM reduction achieved was greater than the 90th percentile of the projects in the 235-site database (90th percentile = 2.7 OoMs). As commonly observed for bioremediation sites in the 235-site database where poorer levels performance was achieved when considering total CVOCs, the results at this site showed significant increases in concentrations of daughter products cis-DCE and vinyl chloride.

Concentrations of geochemical parameters remain indicative of on-going bioremediation, with elevated levels of total organic carbon (TOC), methane, alkalinity, manganese, and ferrous iron compared to baseline conditions, and depressed levels of sulfate and nitrate. The TOC level of 93 mg/L (69 mg/L dissolved TOC) indicates that bioremediation processes could remain on-going for some time at this site. Total biomass concentrations in the most recent sample remained significantly elevated above baseline conditions, but notably the sample was non-detect for *Dehalococcoides sp.* This could explain the absence of ethene and ethane in the sample. Overall, the results appear to support on-going bioremediation, or sustained treatment, at this site. Further statistical analysis of the results is provided in Section 5.1.2.

5.1.1.2 Tinker AFB Results for DRA

At the Tinker AFB Driving Range Area, groundwater samples were collected from 4 monitoring wells located within the former treatment zones (see Figure 5.2). Groundwater in this area was treated via injections of lactate, Fenton's reagent, and permanganate in 2003-2004. Post-treatment groundwater samples were collected throughout numerous sampling events in 2003 and 2004. In 2006, researchers from Oklahoma State University conducted a follow-up sampling event (Scott et al., 2011). Following this sampling event, the test wells were plugged and abandoned.

Because this site offered a unique ability to perform long-term post-treatment testing of 3 remedial applications in the same hydrogeologic setting, new monitoring wells were installed within the 3 former test plots for the purposes of long-term post-treatment groundwater sampling. A sample was also collected from an existing well, 2-348B, located outside of the former treatment zones.

Our long-term post-treatment sampling event was conducted in June 2103, approximately 10 years after treatment and 7 years after the last sampling event. Samples were tested for a broad range of parameters to evaluate the potential for on-going bioremediation (i.e., sustained treatment) vs. rebound. Table 5.3 summarizes the recent sampling results (the only historic results available are for the parent CVOC, TCE). At the request of the Tinker remedial program manager, we also prepared a site investigation report to document our work at Tinker AFB (see Appendix B). This report contains additional details of the sampling and testing program, including monitoring boring logs, laboratory reports, etc.

Figure 5.2. Tinker AFB, Driving Range Area Location Map

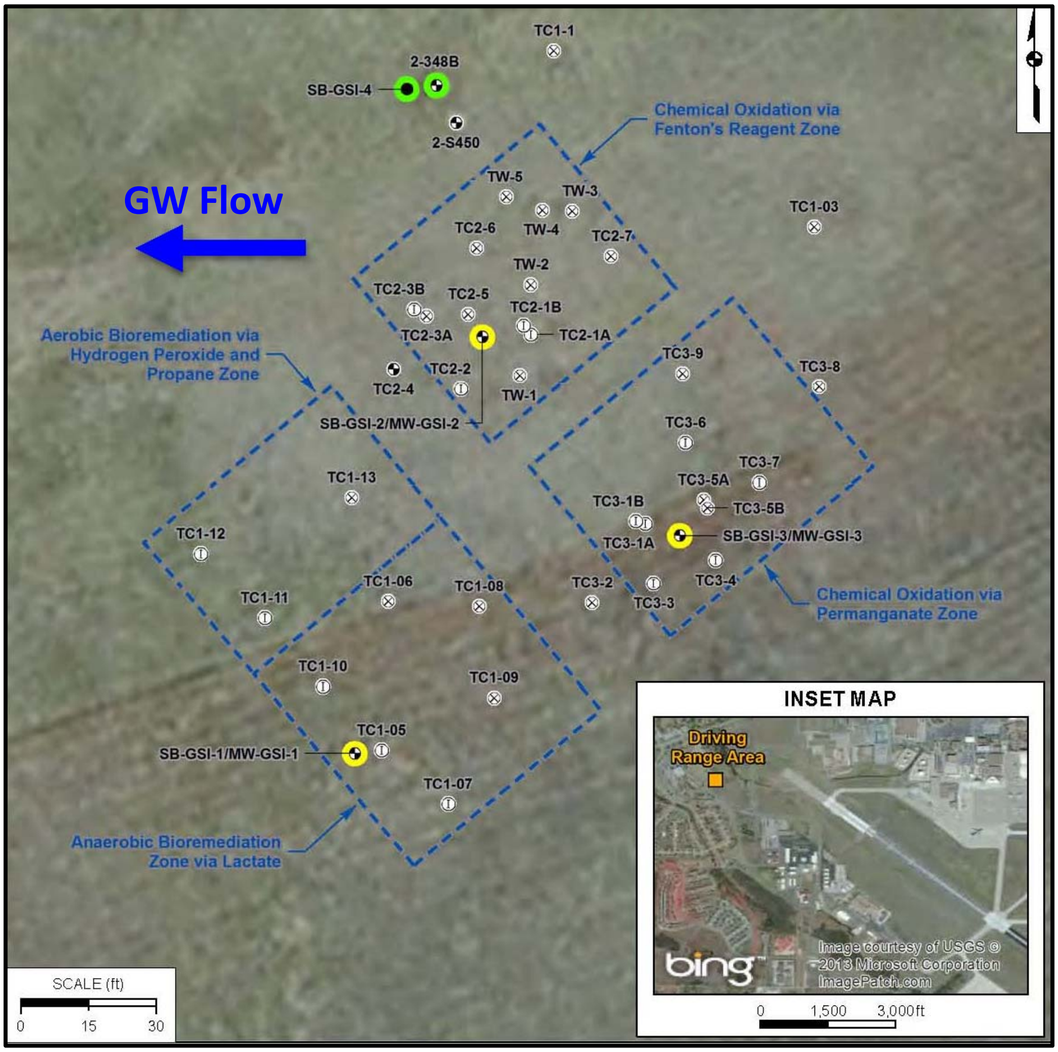


Table 5.2. Recent Groundwater Sampling Results at Tinker AFB, Driving Range Area

Well ID **Former Test Zone** **Former Amendment**	**MW-GSI-1** **Bioremed.** **Lactate**	**MW-GSI-2** **Chem. Ox.** **Fenton's**	**MW-GSI-3** **Chem. Ox.** **KMnO4**	**2-348B** **Untreated** **None**
Sample Date	**11/16/2013**	**11/16/2013**	**11/16/2013**	**11/15/2013**
Chlorinated VOCs	mg/L	mg/L	mg/L	mg/L
Tetrachloroethene	**0.0011**	**0.0015**	**0.0018**	**0.0017**
Trichloroethene	**1.3**	**0.12**	**0.36**	**0.71**
cis-1,2-Dichloroethene	**0.054**	**0.017**	**0.026**	**0.029**
trans-1,2-Dichloroethene	**0.0036**	**0.00062 J**	**0.00077 J**	**0.00046 J**
Vinyl chloride	<0.0010	<0.0010	<0.0010	<0.0011
Organic Compounds	mg/L	mg/L	mg/L	mg/L
Methane	<0.010	<0.010	<0.010	<0.010
Ethane	<0.013	<0.013	<0.013	<0.013
Ethene	<0.013	<0.013	<0.013	<0.013
Acetylene	<0.021	<0.021	<0.021	<0.021
Total Organic Carbon	**0.61 J**	**0.83 J**	**0.78 J**	**1.2**
Dissolved Organic Carbon	**0.74 J**	**0.91 J**	**0.66 J**	**8.1**
Inorganic Compounds	mg/L	mg/L	mg/L	mg/L
Calcium, Dissolved	**110**	**100**	**100**	**130**
Iron, Dissolved	<0.10	<0.10	**0.42**	<0.10
Magnesium, Dissolved	**41**	**36**	**38**	**51**
Manganese, Dissolved	<0.010	0.0082	**0.022**	<0.010
Potassium, Dissolved	**1.1**	**0.66**	**1.1**	**0.48**
Sodium,Dissolved	**50**	**65**	**53**	**45**
Chloride	**70**	**58**	**58**	**59**
Nitrate	**2.6**	**0.52**	**1.2**	**0.56**
Sulfate	**8.1**	**12**	**11**	**91**
Alkalinity, as CaCO3	**400**	**440**	**420**	**440**
Field Parameters				
Temperature, degrees C	18.64	19.84	20.43	17.79
pH	6.88	6.82	6.89	6.72
Specific Conductance, mS/cm	1.04	1.04	1.01	1.14
Turbidity, NTU	692	288	>1000	24.1
Dissolved Oxygen, mg/L	5.67	3.02	2.47	4.65
Oxidation-Reduction Potential, mV	79	175	118	184
Ferrous Iron, mg/L	1.31	0.12	0.99	0.46

Former Bioremediation Test Plot Results

Historic pre-treatment concentrations of TCE in this plot area were approximately 1.2 mg/L. Average TCE concentrations immediately after treatment had declined by about 0.2 OoM (40% reduction). At 2 years after treatment, TCE was not detected at a detection limit of 0.01 mg/L (Scott et al., 2011). Using one-half the detection limit as a surrogate for the non-detect sample, results in an overall 2.2 OoM reduction (99.3%) at 2 years post-treatment. Current results indicate that TCE has rebounded, with a concentration in well GSI-MW-01 reported at 1.3 mg/L. The geochemical groundwater data also are not indicative of on-going bioremediation.

In addition to groundwater samples, soil samples were also collected during installation of the monitoring well at the former bioremediation plot (the soil boring ID was SB-GSI-1). Soil samples within the former injection zone were tested for TCE, Potentially-Bioavailable Organic Carbon (PBOC), and Aqueous and Mineral Intrinsic Bioremediation Assessment (AMIBA) parameters. The objective of the soil samples was to determine whether the substrate injections had resulted in any change in the organic carbon or geochemical makeup of the soil that could result in sustained treatment or enhanced natural attenuation. Soil samples were also collected and tested for the same parameters in a soil boring (SB-GSI-4) installed adjacent to the untreated well location. The soil sampling results are illustrated on Figure 5.3 (TCE and PBOC) and Figure 5.4 (TCE and AMIBA), and are discussed in further detail below.

PBOC results in the former treatment zone (SB-GSI-1) were compared to results in the untreated zone (SB-GSI-4) to determine if PBOC results were higher in the treated zone, as hypothesized. Each soil boring contained six samples (i.e., $n = 6$). The statistical ProUCL software (version 5.0.00) was used to compare the analytical results from these borings with a parametric unpaired pooled t-test and nonparametric Wilcoxon-Mann-Whitney test. Both the t-test ($p = 0.951$) and the Wilcoxon-Mann-Whitney test ($p = 0.954$) indicate that the PBOC results in the treated boring (SB-GSI-1) were significantly greater than the PBOC results in the untreated boring (SB-GSI-4) at a 95% confidence level.

The various AMIBA parameters were also tested with the t-test and Wilcoxon-Mann-Whitney test in ProUCL. Only strong acid soluble ferric iron showed a statistically significant difference between the treated (SB-GSI-1) and untreated (SB-GSI-4) soil borings at a 90% confidence level ($p = 0.93$ with the pooled t-test; $p = 0.926$ with the Wilcoxon-Mann-Whitney test). Strong acid soluble ferrous iron and bioavailable ferric iron were not significantly different between the treated (SB-GSI-1) and untreated borings (SB-GSI-4); each p-value was less than 0.90. Acid volatile sulfide, chromium extractable sulfide, oxidized iron, and pre-incubated reduced iron were not tested statistically because the majority of the data was below the laboratory reporting limit.

Together, the soil sampling results indicate a potential for on-going enhanced attenuation at the soil mineral surface. This could explain why TCE soil concentrations in the former treatment zone are generally lower than those reported in the untreated soil boring. However, based on the groundwater results, the capacity for continued degradation on the soil surface does not appear to be great enough to overcome the inflow of TCE-containing groundwater at the site.

Figure 5.3. Soil Sampling Results for TCE and PBOC at Tinker AFB, Driving Range Area Former Bioremediation Test Plot and Untreated Location

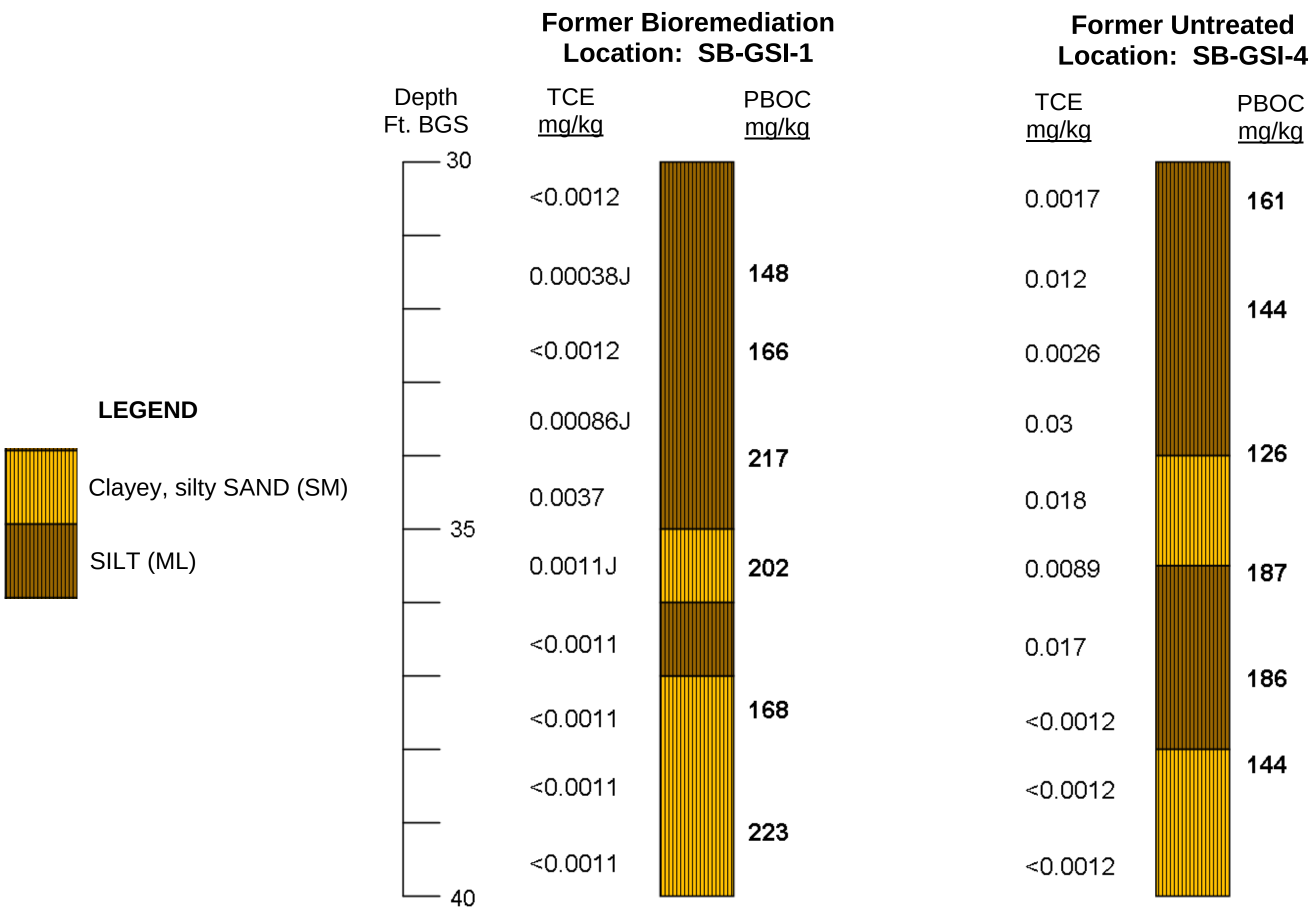
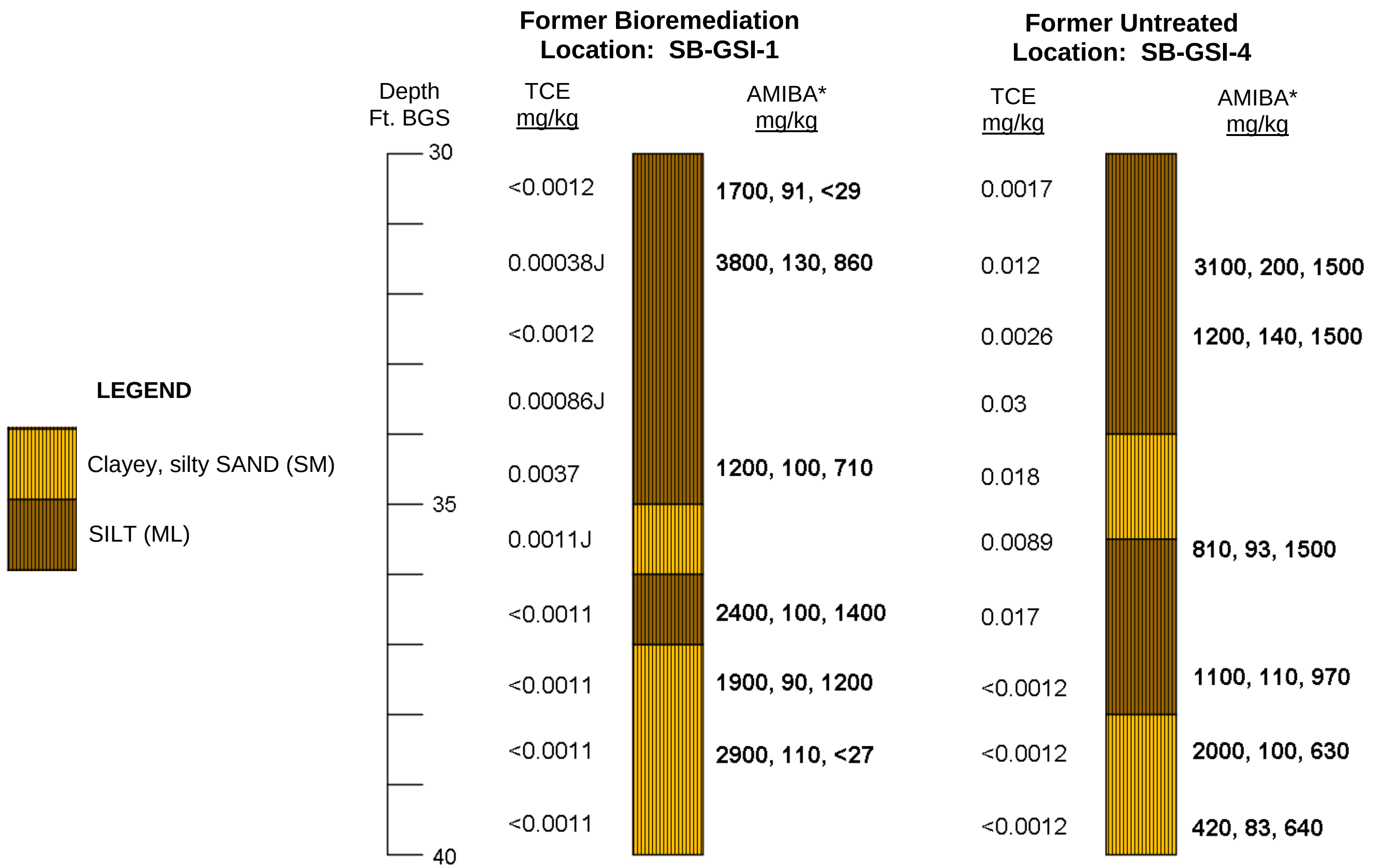


Figure 5.4. Soil Sampling Results for TCE and AMIBA at Tinker AFB, Driving Range Area Former Bioremediation Test Plot and Untreated Location



* AMIBA parameters are as follows: Strong acid soluble ferric iron, Strong acid soluble ferrous iron, and Bioavailable ferric iron

Former Chemical Oxidation (Fenton's Reagent) Test Plot Results

The historic pre-treatment concentration of TCE in this plot area was approximately 1.2 mg/L. Average TCE concentrations immediately after treatment had declined by about 0.9 OoM (88% reduction). At 2 years after treatment, the geomean TCE concentration was approximately 0.038 mg/L (Scott et al., 2011) in this plot, resulting in an overall 1.5 OoM reduction (97%) at 2 years post-treatment. Current results indicate that TCE remains depressed in this plot, with a concentration in well GSI-MW-02 reported at 0.12 mg/L, indicating an overall 1 OoM (90%) reduction.

Former Chemical Oxidation (Potassium Permanganate) Test Plot Results

The historic pre-treatment concentration of TCE in this plot area was approximately 0.4 mg/L, slightly lower than the other test plots. Average TCE concentrations immediately after treatment had declined by about 0.6 OoM (73% reduction). At 2 years after treatment, TCE was not detected at a detection limit of 0.01 mg/L (Scott et al., 2011). Using one-half the detection limit as a surrogate for the non-detect sample, results in an overall 1.9 OoM reduction (98.8%) at 2 years post-treatment. Current results indicate that TCE has rebounded in this plot, with a concentration in well GSI-MW-03 reported at 0.36 mg/L, which is consistent with pre-treatment levels.

5.1.1.2 Altus AFB Results for Building 323

At Altus AFB Building 323, groundwater samples were collected from 3 monitoring wells: 2 within the former bioremediation treatment zone and 1 upgradient well located upgradient of the former treatment zone (see Figure 5.5). Groundwater in this area was treated via injections of emulsified vegetable oil in August 2008. Post-treatment groundwater samples were collected during two sampling events in November 2009 and May 2010. Our long-term post-treatment sampling event was conducted in June 2103, almost 5 years after treatment and more than 3 years after the last sampling event. Samples were tested for a broad range of parameters to evaluate the potential for on-going bioremediation (i.e., sustained treatment) vs. rebound. Table 5.3 summarizes the recent sampling results.

Figure 5.5. Altus AFB, Building 323 Location Map

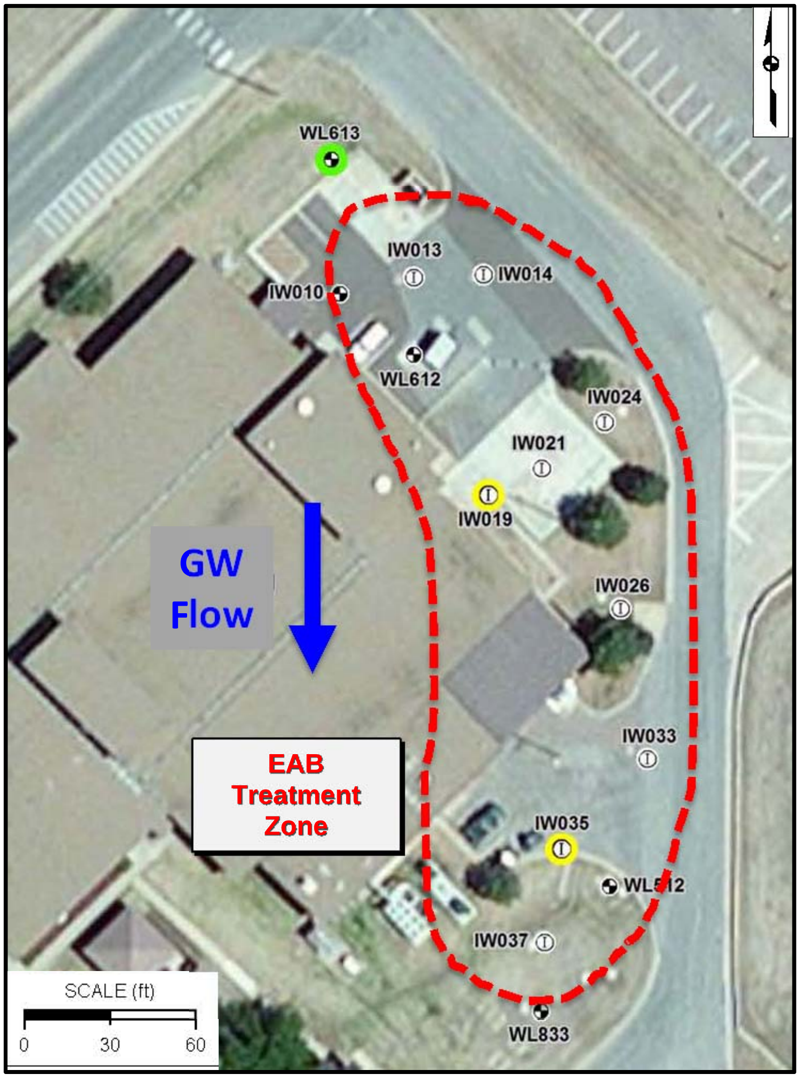


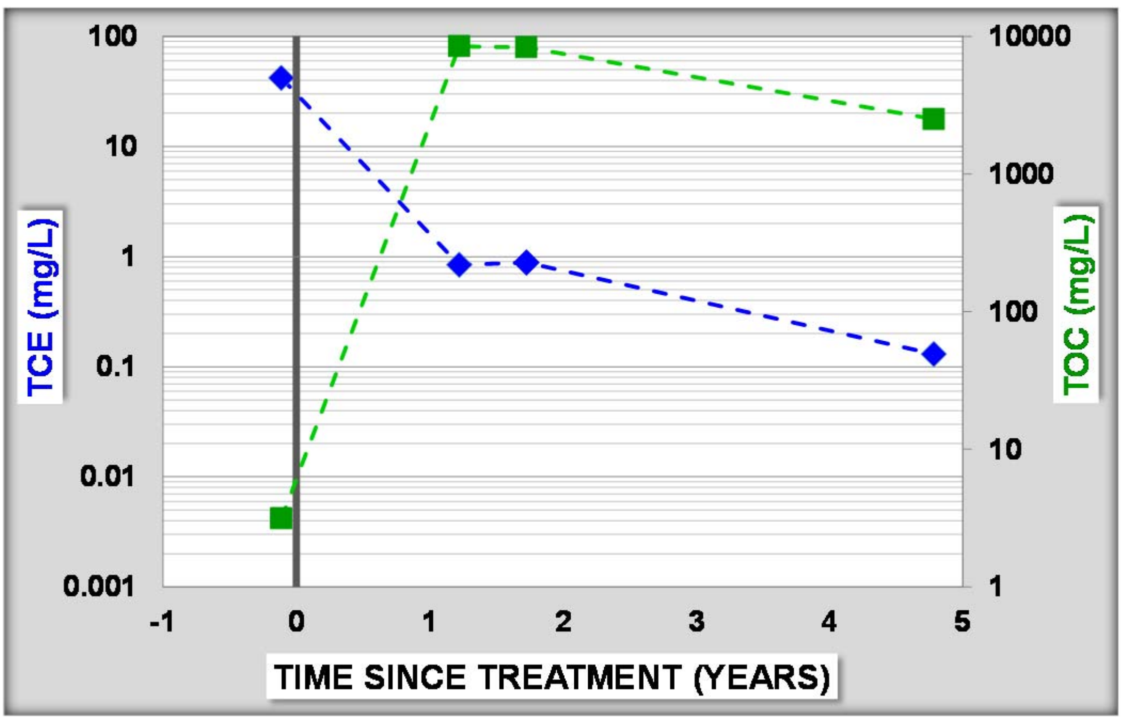
Table 5.3. Recent Groundwater Sampling Results at Altus AFB, Building 323

Site:	Altus	Altus	Altus	Altus
Site ID:	Bldg. 323	Bldg. 323	Bldg. 323	Bldg. 323
Well Location:	Upgradient	Treatment Zone	Treatment Zone	Treatment Zone
Well ID:	WL613	IW019	IW035	DUP-1 (IW035)
Sample Date:	6/5/2013	6/5/2013	6/5/2013	6/5/2013
CVOCs	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Tetrachloroethene (PCE)	<0.00037	<0.00037	<0.00037	<0.00037
Trichloroethene (TCE)	**0.03**	**0.13**	**0.043**	**0.037**
cis-1,2-Dichloroethene (cis-DCE)	**0.0028**	**1.8**	**0.015**	<0.00026
trans-1,2-Dichloroethene (trans-DCE)	<0.0004	**0.0022**	<0.0004	<0.0004
Vinyl Chloride	<0.00026	**0.65**	**0.15**	**0.13**
Dissolved Gases	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Methane	<0.0021	**2.5**	**2.9**	**2.8**
Ethane	<0.004	<0.004	<0.004	<0.004
Ethene	<0.0057	<0.0057	<0.0057	<0.0057
Acetylene	<0.0056	<0.0056	<0.0056	<0.0056
Inorganics	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Chloride	**1400**	**520**	**140**	**140**
Nitrate	**1.7**	<0.023	<0.023	**0.096 J**
Sulfate	**2700**	**0.48 J**	**7.1**	**9.5**
Alkalinity	**200**	**120**	**1300**	**1200**
Calcium	**400**	**180**	**190**	**190**
Iron	**0.052 J**	**47**	**1.6**	**1.9**
Magnesium	**150**	**240**	**96**	**97**
Potassium	**8.1**	**9.5**	**3.4**	**3.4**
Sodium	**810**	**790**	**300**	**300**
Organic Carbon	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Total Organic Carbon	**1.3**	**--**	**54**	**--**
Dissolved Organic Carbon	**1.1**	**2,500**	**46**	**43**
Microbial				
DNA (µg/L)	**13.7**	**30.0**	**42.9**	**37.7**
DhC (cells/L)	<3 E+3	1 E+9	5 E+7	6 E+7

As shown on Figure 5.6, pre-treatment TCE concentrations were approximately 42 mg/L. Within 2 years after treatment, TCE concentrations had declined to approximately 0.8 mg/L, representing a 1.7 OoM reduction. Our sampling results, nearly 5 years post-treatment, indicated that TCE declined by an additional 0.7 OoMs, resulting in a total reduction of approximately 2.4 OoMs. These results suggest better than average performance was achieved initially by the remediation project, and after 10 years, the OoM reduction achieved was between the 75th and 90th percentiles of the projects in the 235-site database (75th to 90th percentile range = 2.0 to 2.7 OoMs). As commonly observed for bioremediation sites in the 235-site database where poorer levels performance was achieved when considering total CVOCs, the results at this site showed significant increases in concentrations of daughter products cis-DCE and vinyl chloride.

Concentrations of geochemical parameters remain indicative of on-going bioremediation, with elevated levels of total organic carbon (TOC), methane, alkalinity, manganese, and ferrous iron compared to upgradient conditions, and depressed levels of sulfate and nitrate. The TOC levels of 54 mg/L and 2,500 mg/L indicate that bioremediation processes could remain on-going for some time at this site. Samples collected within the treatment zone also contained significant concentration of *Dehalococcoides sp.* Despite the presence of these organisms, ethene and ethane were not detected. Overall, the results appear to support on-going bioremediation, or sustained treatment, at this site. Further statistical analysis of the results is provided in Section 5.1.2.

Figure 5.6. TCE and TOC Concentrations Over Time Within the Former Treatment Zone at Altus AFB, Building 323, Well IW019



5.1.2 Statistical Analysis Results

5.1.2.1 Objectives

The primary objective of this statistical evaluation of post-treatment concentration data was to determine long-term remediation performance is maintained (sustained treatment). In each case, an indicator for sustained treatment was when a result is similar to, or better than, the result that was obtained prior to the inclusion of new data from the current long-term post-treatment monitoring period. Failure to obtain the same or better result was an indicator of concentration rebound.

5.1.2.2 Technical Approach

A separate evaluation was performed using the data from 6 monitoring wells: IW019, IW035 (Altus AFB), SIW01, MWGSI01, MWGSI02, MWGSI03 (Tinker AFB). The same methodology was used for each well:

(1) The average parent concentration in the post-treatment period including the new monitoring data was calculated and compared to the average parent concentration in the post-treatment period without the new monitoring data (i.e., historic post-treatment data only). Note that because the two groups of data were not independent, there was no attempt to compare the mean values using a t-test (or a Wilcoxon Rank Sum for the median values).

(2) The trend in the parent concentration during the post-treatment period including the new monitoring data was assigned using the Mann-Kendall test, and then compared to the trend for the post-treatment parent concentration data excluding the new monitoring data. Note that a minimum of 4 data points are required for the Mann-Kendall test, and several wells did not meet this requirement.

(3) Linear regression was used as a second method for comparing the trend in the parent concentration during the post-treatment period including the new monitoring data relative to the post-treatment trend without the new monitoring data. In this case, the sign of the slope of the best-fit regression line was used an indicator (i.e., if the slopes of both regression lines were negative, then the same performance was confirmed).

5.1.2.3 Results

Table 5.4 summarizes the results of the evaluation. For 5 of the 6 wells, each of the three lines of evidence (described above) supported that sustained treatment was occurring: IW019, IW035, SIW01, MWGSI02, and MWGSI03. This set of wells contains 3 from areas treated with enhanced bioremediation and 2 from areas treated with chemical oxidation. For the remaining well, MWGSI01, the Mann-Kendall trend changed from Probably Decreasing to Stable when the new monitoring data. The average post-treatment concentration also increased slightly when the new monitoring data was included for this well. It should be noted that for MWGSI01, the historic post-treatment monitoring record contains one data point that is much lower than either

the preceding historic concentration data or the most recent concentration (from this field demonstration).

5.1.2.4 Conclusions of Statistical Analysis

Sustained treatment was confirmed at 5 of the 6 wells that were evaluated. The sixth well still exhibited a stable trend during the post-treatment period, but a decreasing trend was exhibited prior to the addition of the new data point. The type of remediation performed did not have a clear influence on whether or not sustained treatment was observed.

Table 5.4. Evaluation of Concentration Trends During Post-Treatment Period

Site and Well ID	Technology	Constituent	Average Post-Treatment Conc. – Historic Data Only (mg/L)	Average Post-Treatment Conc. – Historic & New Data (mg/L)	Is Trend Better?	Mann-Kendall Trend – Historic Data Only (mg/L)	Mann Kendall Trend – Historic & New Data (mg/L)	Is Trend Better?	Linear Regression Trend – Historic Data Only (mg/L)	Linear Regression Trend – Historic + New Data (mg/L)	Is Trend Better?
Altus IW019	Enh. Bio.	TCE	0.863	0.618	**YES**	N/A	N/A	N/A	Increasing	Decreasing	**YES**
Altus IW035	Enh. Bio.	TCE	1.382	0.935	**YES**	N/A	N/A	N/A	Decreasing	Decreasing	**YES**
Tinker FTA2 SIW01	Enh. Bio.	TCE	0.060	0.046	**YES**	N/A	Stable	N/A	Increasing	Decreasing	**YES**
Tinker DRA MWGSI01	Enh. Bio.	TCE	1.029	1.039	**NO**	Prob. Decreasing	Stable	**NO**	Decreasing	Decreasing	**YES**
Tinker DRA MWGSI02	Chem. Ox.	TCE	0.481	0.472	**YES**	Decreasing	Decreasing	**YES**	Decreasing	Decreasing	**YES**
Tinker DRA MWGSI03	Chem. Ox.	TCE	0.340	0.340	**NO**	Decreasing	Decreasing	**YES**	Decreasing	Decreasing	**YES**

Notes: (1) Post-treatment concentrations include all measurements after the start of treatment (including those events completed while treatment was on-going; (2) N/A = not applicable due to only 3 data points; Mann-Kendall trend analysis requires a minimum of 4 data points.

5.2 Analysis of "Remediation Done Right" Sites

To get an independent perspective on in-situ remediation performance, a quick survey for three well-implemented, well-reported peer-reviewed remediation projects was performed and summarized below. These projects represent "remediation done right" for individual one-phase treatment projects (i.e., treatment trains are excluded from this analysis). The focus is on what is the performance for well-designed, well executed, and well-documented in-situ remediation projects in the scientific literature.

Project 1: Permanganate Treatment of an Emplaced DNAPL Source (Thomson et al., 2007). In this project, an emplaced DNAPL source was treated with permangate in-situ chemical oxidation via groundwater recirculation. Because 1) the source was emplaced, and 2) because of previous research activities this aquifer and relatively simple sandy geology, it one of the best-understood formations in the world and the overall degree of knowledge about the remediation problem was extremely high. The recirculation treatment project was conducted over 485 days, and performance was characterized with 99 piezometers and 23 before- and after-treatment core locations.

Results: Overall, greater than 99% of the mass in the source zone was removed, and the mass discharge was reduced by 99% (2 OoMs) for TCE and 89% (about 1 OoM) for PCE (Table 5.5). However, the maximum concentration of TCE in the treatment zone was only reduced by 84% and PCE only 50%. The authors concluded *"In addition, the manner in which this source zone was constructed represents perhaps a best-case condition for dissolution. Given these clear advantages relative to actual contaminated sites and the lengthy period of permanganate injection (485 d), there remained a distinct chloroethene plume 400 d after active permanganate treatment was terminated. The presence of this remaining plume under these near-ideal treatment conditions suggests that partial source mass removal is a likely outcome of permanganate treatment, and hence, performance expectations should be accordingly tempered."*

Table 5.5 Summary of Treatment Performance Metrics University of Waterloo Permanganate Treatment of an Emplaced DNAPL Source (Thomson et al., 2007)

	Baseline		Post-Treatment		Percent Reduction	
	TCE	PCE	TCE	PCE	TCE	PCE
Peak Concentration (**mg/L**)	140	60	22.0	30	84	50
Ambient-gradient loading (**mg/d**)	860	880	7.0	98	99	89
Forced-gradient loading (**mg/d**)	2100	2220	17	220	99	90
Mass in source zone (**Kg**)	9.0	1.6	<0.001	<0.001	>99	>99

Project 2: Full Scale Remove of DNAPL Constituents Using Steam-Enhanced Extraction and Electrical Resistance Heating (Heron et al., 2005). A 12,900 cubic yard treatment zone at a Dept. of Energy site in a fine-grained sand aquifer was treated using both steam injection

electrical resistance heating over a 4.5 month period. The treatment system was comprised of 15 steam injection wells; 28 extraction wells with electrodes, 21 combined steam/electrode wells, 2 deep electrodes into the underlying clay, 36 temperature monitoring boreholes, and four pairs of groundwater monitoring wells. The constituents of concern for this site were TCE, toluene, cis-1,2-dichloroethylene (cis-1,2-DCE), methylene chloride, and petroleum range organics. The source zone was estimated to contain approximately 2600 pounds of volatile organic compounds.

Results: Groundwater concentrations of the four constituents were reduced by approximately 3 OoMs (99.9%) based on data for the four CVOCs from before and after treatment (Table 5.6). Mass removal for the four individual constituents was estimated between 3 and 4 OoMs (99.9% to 999.9%), while an estimated 61% of the total petroleum hydrocarbons were removed based on soil sampling data. Post-treatment sampling data showed "all concentrations to be below or close to ground water MCLs."

A retrospective analysis of remediation case studies by Dr. Jim Mercer (Mercer, 2010) summarized this project this way: *"For Northeast Area A, using steam to deliver heat to the permeable zones and electrical heating for the low-K Hawthorn clay lead to effective heating of the treatment zone for this small and accessible source zone; the larger Northeast Area B required additional remediation following thermal treatment."* However, he went on to note that the off-site plume from the complex is currently being investigated and that for a sister site (Area B), thermal did not remove all the source material: *"(In 2005) thermal (was) applied to Area B ending after about 12 months on August 29, 2006; subsequent soil borings identified two areas still containing contaminant source material. (In 2009) about 8,387 cubic yards of soil excavated via large-diameter auger (LDA) using 243 LDA and 352 small-diameter augers. A planned follow up to the LDA is enhanced bioremediation."*

Table 5.6 Remediation Performance Data for Dept. of Energy Thermal Treatment Project – Reduction in Groundwater Concentrations (Heron et al., 2005)

	Maximum Concentration Before-Treatment (µg/L)	Maximum Concentration After-Treatment (µg/L)	Percent Reduction	OoM Reduction
cis-1,2 dichlorethene	17,000	76	99.6%	2.4
Methylene Chloride	12,000	12	99.9%	3.0
Toluene	22,000	23	99.9%	3.0
Trichloroethene	37,000	12	99.97%	3.5
Petroleum Range Organics	(No value provided)	9500	-	-

Project 3. Demonstration of Enhanced Bioremediation in a TCE Source Area at Launch Complex 34, Cape Canaveral Air Force Station (Hood et al., 2008). A bioremediation pilot test was conducted within the upper portion of an unconfined sandy aquifer (depth to water 10 feet bgs) that was composed of medium to coarse-grained sand and crushed shells. The Pilot Test was performed with three injection wells and three extraction wells over a 20 foot by 20 foot test plot; vertically the test plot extended to 26 feet bgs. After 78 days of circulating unamended groundwater, biostimulation was performed for 108 days until a bioaugmentation step was performed. After the single bioaugmentation step, biostimulation was performed for an additional 249 days. The electron donor addition consisted of weekly 5 minute pulses of 10% denaturated alcohol into each well with 520 mg/L of enthanol. Bioaugmentation was performed by injecting 13 liters of KB-1 formulation.

Results: In the coarse-grained upper sand unit, the maximum TCE concentration was reduced from an average of 155 ug/L TCE and 158 ug/L of total chlorinated ethenes in the center monitoring wells to near non-detect concentrations <0.3 ug/L TCE (>2.7 OoMs) but with 108 ug/L of daughter products remaining after the end of the treatment. Detailed soil sampling indicated that approximately 98.5% (about 2 OoMs) of the source zone mass was removed.

However after about two years after the pilot test terminated, post-demonstration sampling indicated sustained treatment may have been on-going, with average TCE concentrations dropping to non-detect concentrations (<0.05 ug/L) and total chlorinated ethenes declining to 1.8 ug/L (a 1.9 OoM reduction).

Table 5.7. Remediation Performance Data for Cape Canaveral Thermal Treatment Project – Reduction in Groundwater Concentrations After Each Phase (Hood et al., 2008).

Parameter	*Baseline*	*Biostimulation*	*Bioaugmentation*	*Post-Demonstration*
Chloride (mg/L)	182 (164 to 197)	185 (170 to 190)	NS	NS
Nitrate-N (mg/L)	<0.6	<0.6	<0.6	NS
Sulfate (mg/L)	315 (286 to 351)	2 (<0.2 to 4)	8 (<0.2 to 11)	NS
Orthophosphate (mg/L)	<4	NS	<4	NS
Trichloroethene	155 (100 to 210)	35 (6 to 90)	<0.3 (<0.2 to 0.5)	Not detected (<0.05)
cis-1,2-Dichloroethene	3 (2 to 4)	84 (55 to 99)	29 (<0.5 to 48)	0.8 (0.02 to 3)
Vinyl Chloride	<0.2 (<0.05 to 0.5)	24 (15 to 37)	53 (14 to 110)	1 (0.06 to 4)
Ethene	<0.2 (<0.05 to <0.5)	2 (0.9 to 4)	67 (26 to 92)	4 (1 to 7)
Methane	0.4 (0.1 to 1.1)	0.6 (0.6 to 0.6)	14 (11 to 21)	14 (10 to 18)

Note: Centerline wells were averaged (MW03, PA-26, W-6, and FL-2). Groundwater sampling dates for VOCs: (Baseline 2-Oct-03; Biostim 7-Feb-03; Bioaug 14-Oct-03; Post-Demo 16-Aug-05)

Overall Conclusion: In summary, the results reported for these three projects indicated that two of three sites outperformed many of the sites in the 235 site database (achieving parent CVOC reductions of 2.7 and 3.5 OoMs, greater than the 90% percentile of the 235 site dataset), while the third site had a result more comparable to the median of the 235 site dataset with a 0.8 OoM reduction (the median reduction of the 235 site dataset was 1.1 OoM).

5.3 Analysis of Treatment Train Sites

14 projects in the database implemented 2 different in-situ technologies in sequence within the same treatment zone. These are commonly referred to as “treatment train” sites. These sites were examined in additional detail to evaluate whether successively applied technologies result in better performance than a single technology.

As summarized on Table 5.8 below, all of these sites incorporated bioremediation as 1 of the technologies. Chemical oxidation was implemented at 12 of the 14 sites, with thermal and surfactant each being used at 1 site each.

Table 5.8. Technology Summary at Treatment Train Sites

Site ID	Tech 1	Amendment	Tech 2	Amendment
TT-1	Bioremediation	Slow-release	Chem. Ox.	Persulfate
TT-2	Bioremediation	Slow-release	Chem. Ox.	Permanganate
TT-3	Bioremediation	Slow-release	Chem. Ox.	Permanganate
TT-4	Bioremediation	Slow-release	Chem. Ox.	Persulfate
TT-5	Bioremediation	Soluble	Chem. Ox.	Fenton’s Reagent
TT-6	Chem. Ox.	Fenton’s Reagent	Bioremediation	Soluble
TT-7	Chem. Ox.	Permanganate	Bioremediation	Slow-release
TT-8	Chem. Ox.	RegenOx	Bioremediation	Slow-release
TT-9	Chem. Ox.	Permanganate	Bioremediation	Slow-release
TT-10	Chem. Ox.	Fenton’s Reagent	Bioremediation	Slow-release
TT-11	Chem. Ox.	Fenton’s Reagent	Bioremediation	Soluble
TT-12	Chem. Ox.	Permanganate	Bioremediation	Slow-release
TT-13	Surfactant	Tween 80	Bioremediation	Slow-release
TT-14	Thermal	ERH	Bioremediation	Soluble

5.3.1 What Happened After the First Treatment?

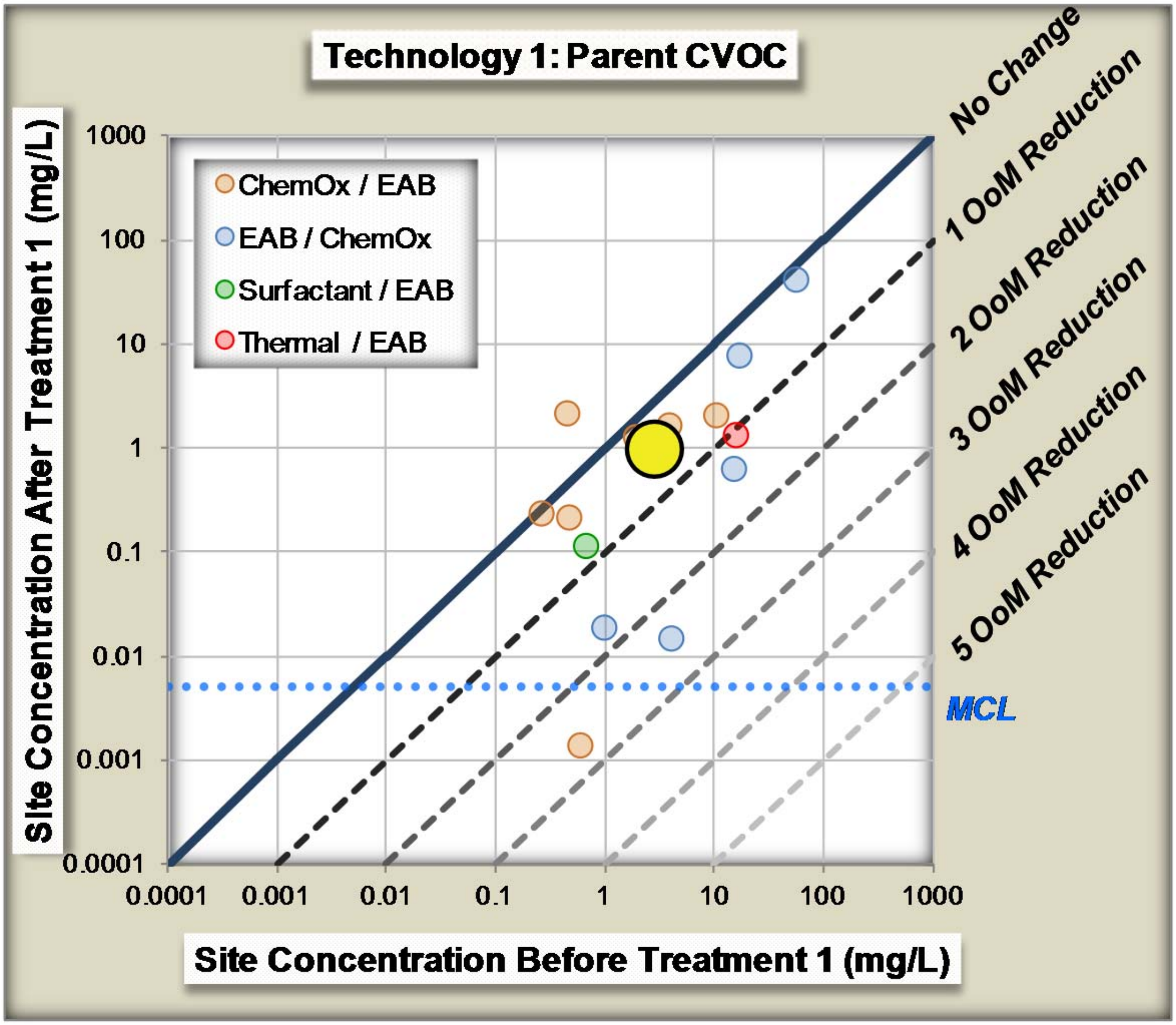


Figure 5.7. Performance Achieved After the 1st Technology at 14 Treatment Train Sites

Data Shown: *Parent compound geomean concentration before and after the 1st technology. The different color dots represent different technology combinations.*

Explanation: *Each dot represents an individual project, showing the geomean before treatment concentration (X-axis) and after treatment concentration, but before the 2nd treatment was implemented (Y-axis). The yellow circle represents the median of all 14 sites.*

Key Points

- The first technology at treatment train sites achieved only about a 0.5 OoM reduction based on the median of all 14 sites. This is lower than the median OoM reduction of 1.1 observed for all 235 of the remediation projects.

5.3.2 *What Happened After the Second Treatment?*

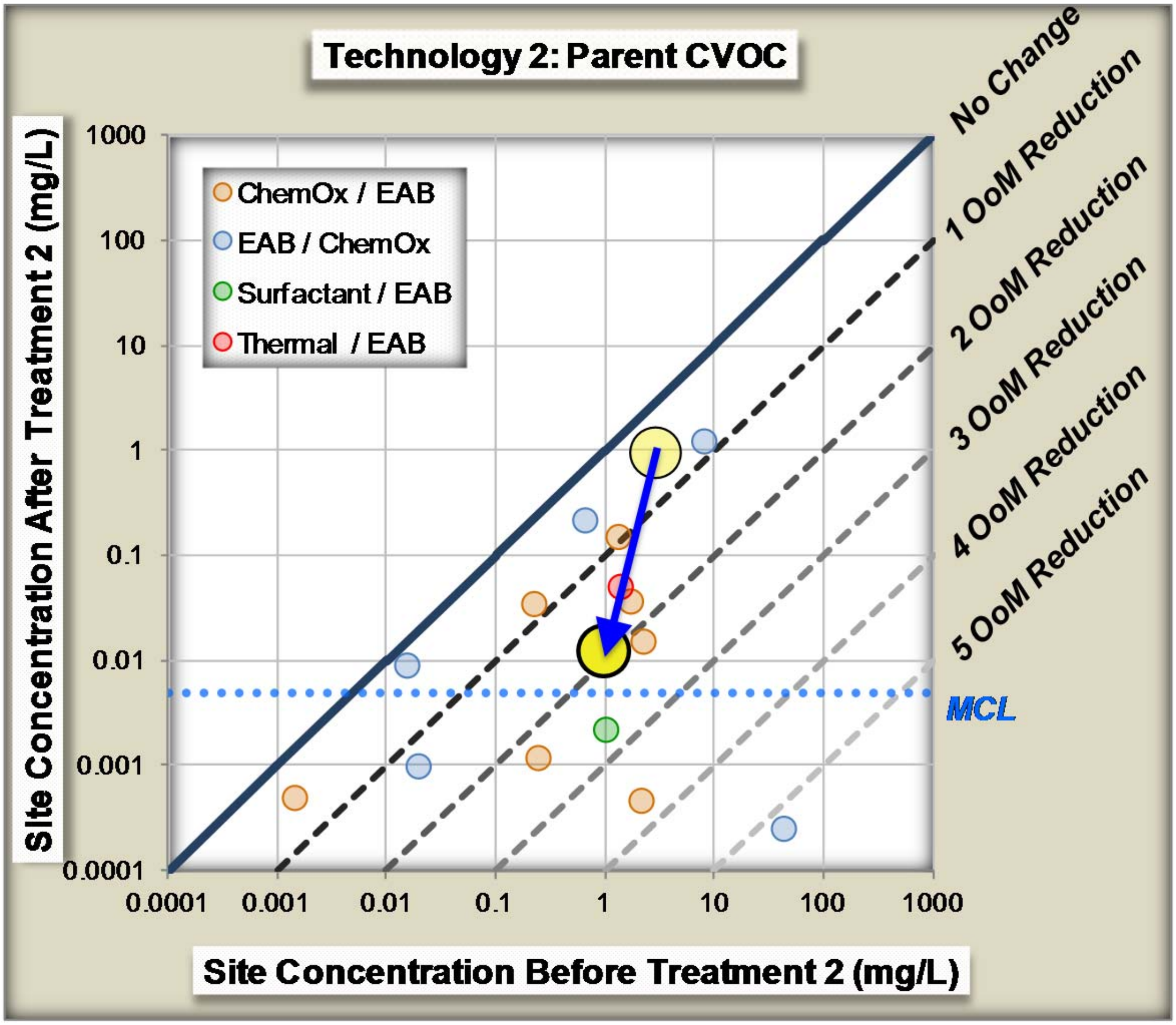


Figure 5.8. Performance Achieved After the 2nd Technology at 14 Treatment Train Sites

Data Shown: *Parent compound geomean concentration before and after the 2nd technology. The different color dots represent different technology combinations.*

Explanation: *Each dot represents an individual project, showing the geomean concentration before the 2nd treatment was implemented, but after the 1st technology (X-axis) and after the 2nd treatment (Y-axis). The yellow dark circle represents the median of all 14 sites.*

Key Points

- The second technology at treatment train sites achieved about a 2 OoM reduction based on the median of all 14 sites. This is higher than the median OoM reduction of 1.1 observed for all 235 of the remediation projects.

5.3.3 What was the Overall Result for Treatment Train Sites?

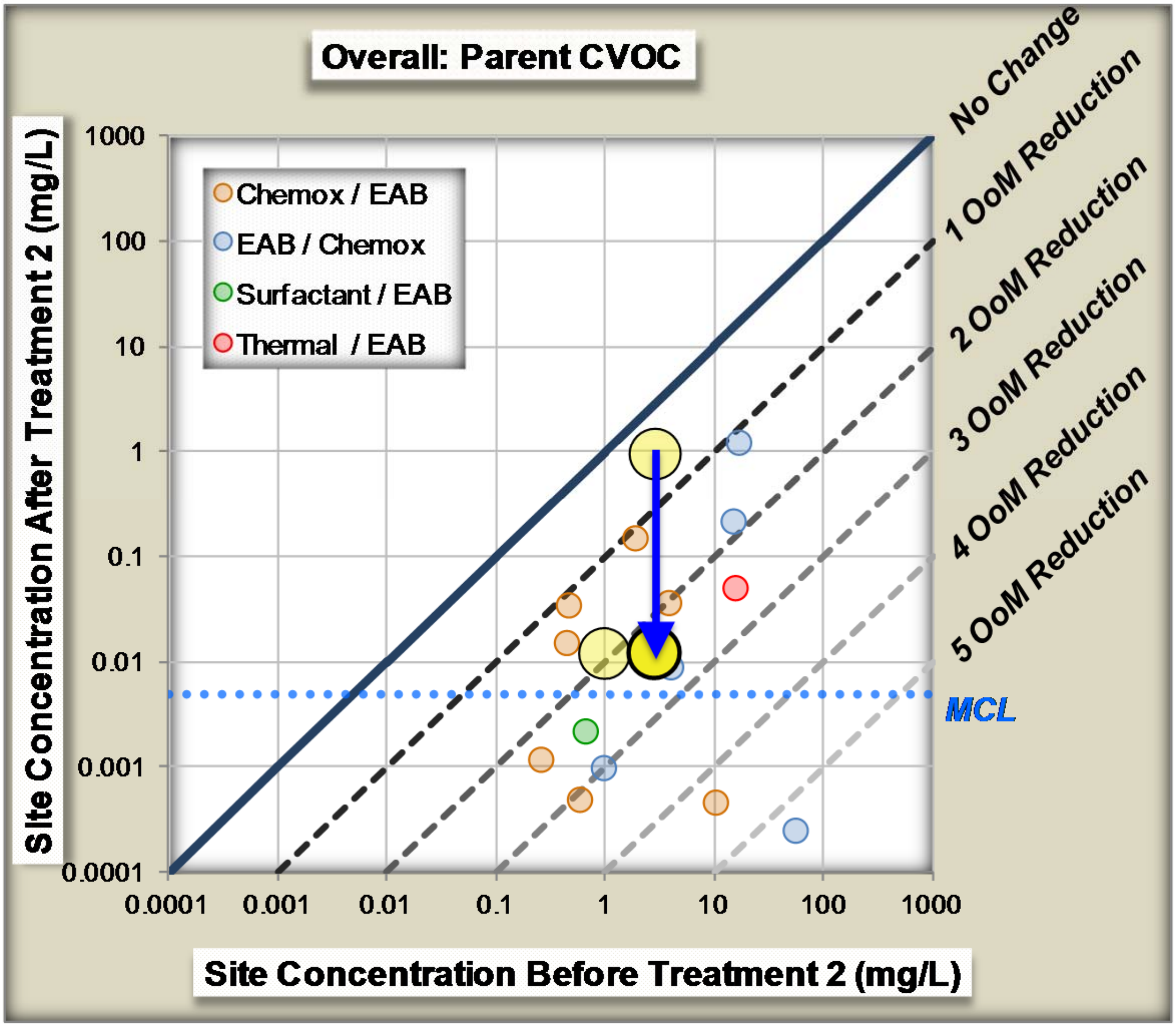


Figure 5.9. Overall Performance Achieved at 14 Treatment Train Sites

Data Shown: *Parent compound geomean concentration before the 1st technology and after the 2nd technology. The different color dots represent different technology combinations.*

Explanation: *Each dot represents an individual project, showing the geomean concentration before any treatment was implemented (X-axis) and after all treatments were complete (Y-axis). The yellow circle represents the all 14 sites.*

Key Points

- Overall the treatment train sites achieved about a 2.3 OoM reduction based on the median of all 14 sites. This is significantly higher than the median OoM reduction of 1.1, as well as the 75th percentile of 2.0 OoM, observed for all 235 of the remediation projects.

- Based on the poor OoM reduction typically achieved by the first technology at these sites (Figure 5.7), it is likely that a key factor in the success of the second technology was the benefit of lessons learned from the first technology implementation.
- Note that one of the treatment train sites achieved the best performance of all 235 projects, with a 5.2 OoM reduction. This site implemented enhanced bioremediation followed by chemical oxidation. Nearly all of the overall OoM reduction achieved at this site was with the chemical oxidation technology, which was implemented after enhanced bioremediation. A more detailed review of the site reports revealed that this was a soil mixing project where the aquifer material was removed, physically mixed with the chemical oxidant, and then returned to the ground. As such, this project was able to overcome many of the inherent limitations associated with injection of amendments, and therefore achieve exceptional results.

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APPENDICES

Appendix A: Expert Panel Meeting Presentation and Follow-Up

Note: The Expert Panel Meeting was held on November 18, 2014. The presentation slides show results that had been compiled at that time.

Appendix B: ESTCP Field Demonstration Site Investigation Report